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Wetting-Out Agents and

Modern Mercerization Methods

By A. J. HALL, B.Sc., F.I.C., F.T.I.

UNTIL comparatively recently, the desizing and other preparation of cotton yarns and fabrics for mercerization played a large part in the successful production of a high luster and soft handle. It was common experience that unless all the starch and fatty impurities associated with cotton materials in the grey were removed, penetration by the caustic soda liquor was retarded and the desirable properties of a well mercerized cotton yarn or fabric were not fully acquired. This is not so today. A number of substances have been discovered which when added to mercerizing liquors in comparatively small proportions have the effect of so greatly increasing their penetrative power that a grey fabric can be mercerized quite as satisfactorily as one which has been fully desized and bleached. The choice as to whether yarn or fabric shall be mercerized in the grey or after desizing is now governed merely by convenience.

It has long been known that the addition of various substances to a mercerizing liquor can materially affect its penetrating properties. Thus the addition of such substances as methyl and ethyl alcohols, aniline, and even turpentine was recommended nearly forty years ago (Ger. Pat. 134449) and in Ger. Pat. 393781 pyridine was suggested as an addition for the purpose of increasing the wetting-out properties of a mercerizing liquor. Most of the substances put forward as being useful proved however to involve some disadvantage. Thus, to have any real effect it is necessary to add at least 20% of ethyl alcohol to a mercerizing liquor and this is obviously prohibitive as regards increased cost. On the other hand, the addition of such substances as aniline and benzene is almost impractical on account of the immiscibility of these organic liquids with caustic soda solutions and also because of their toxic nature. Therefore after a period of experiment with wetting out agents, practically all mercerizers apparently reached the conclusion that it was better to use caustic soda alone and rely for thorough penetration on mechanical devices for securing this.

Some five or six years ago however the search for wetting-out agents for mercerization purposes took a new turn. Phenol was known to be readily soluble in a mercerizing liquor and it was further known that such an addition slightly improved its penetrating properties. But it was then discovered that by mixing quite small amounts of other substances to the phenol, a product could be prepared which had very marked wetting out properties. This discovery was protected by E. P. 279784 and has since led to the most important developments in mercerization.

This early patent claimed that excellent wetting-out agents could be prepared by adding suitable hydrogenated aromatic substances to phenol, cresol, or similar coal tar hydroxy intermediates. Recommended mixtures consisted of 98 to 88% of the phenolic component and 2 to 12% of the hydrogenated compound. Suitable hydrogenated bodies included cyclohexanol and methyl cyclohexanol, and reduction products of naphthalene, naphthols and phenols. Generally it was found sufficient to add but 1 to 2% of the wetting-out agent to the mercerizing liquor in order to secure maximum increase of penetrative power. Typical wetting out agents of this type are:

(1) 91% of commercial cresol mixture
9% of methyl cyclohexanol
and (2) 95% of commercial cresol mixture
5% of tetra-hydronaphthalene

The earlier brands of Mercerol (Sandoz) had a similar composition and some measurements of A. Landolt (Textilber., 1928, *9*, 763) are interesting as showing their beneficial effect in the mercerization of grey cotton yarn.

Landolt's investigations were carried out by plunging a length of cotton yarn into a burette containing a merceriz-

ing liquor (with and without the addition of 1% of Mercerol) and noting the shrinkage in length produced within successive periods of time. His results are given below and also in Figs. 1 and 2.

Grey cotton yarn	**Mercerizing liquor: Caustic soda of 53° Tw.**	
Time after immersion	*Length of Yarn*	
	Without Mercerol	*With Mercerol*
0 minutes	50 cms.	50 cms.
¼	..	45
½	49.65	43.2
¾	..	42.7
1	49.1	42.6
1¼	..	42.5
1½	48.55	42.3
2	48.1	..
3	47.4	..
4	46.90	..
4½	46.75	..

Desized cotton yarn	**Mercerizing liquor as above**	
Time after immersion	*Length of Yarn*	
	Without Mercerol	*With Mercerol*
0 minutes	50 cms.	50 cms.
¼	48.7	46
½	46.2	43.8
¾	44.7	43.5
1	44.0	43.4
1¼	43.6	43.4
1½	43.4	43.4
2	43.2	43.3

It is to be noted that the degree of shrinkage which occurs during mercerization can be assumed to be a measure of the success of the process, that is, the greater the shrinkage the greater can be the expected luster increase. The above results indicate that when Mercerol is present in the caustic soda liquor an amount of shrinkage (about 16%) is obtained with grey yarn which is never secured without Mercerol (about 7%). Also when Mercerol is present it makes little difference whether or not the yarn is first desized. These facts are strikingly shown in Figs. 1 and 2. In Fig. 2 it is useful to note how much the presence of Mercerol increases the rate of shrinkage as compared with the total amount of shrinkage.

Having established the value of phenol mixtures for increasing the penetrating power of a mercerizing liquor it became necessary to examine a wide range of mixtures with a view to discovering those most efficient. Many patents have been taken out covering a number of mixture types and even today improvements are being constantly effected.

It was early discovered (E. P. 350018) that aliphatic and aliphatic-aromatic alcohols and ketone-alcohols could be usefully added to the original phenol-hydrogenated aromatic compound mixtures. Such added ingredients gave increasing wetting-out power and also stability to the alkali-wetting out agent mixture. Suitable aliphatic alcohols proved to be iso-propyl alcohol, iso-butyl alcohol, and amyl alcohol, while benzyl alcohol is an example of a satisfactory aromatic alcohol. The following are typical wetting out agents formed from such mixtures:

(1) 90% of commercial cresol mixture
2½% of methyl cyclohexanol (hydrogenated aromatic compound)
7½% of benzyl alcohol

(2) 90% of commercial cresol mixture
5% of methyl cyclohexanol
5% of Di-acetone alcohol

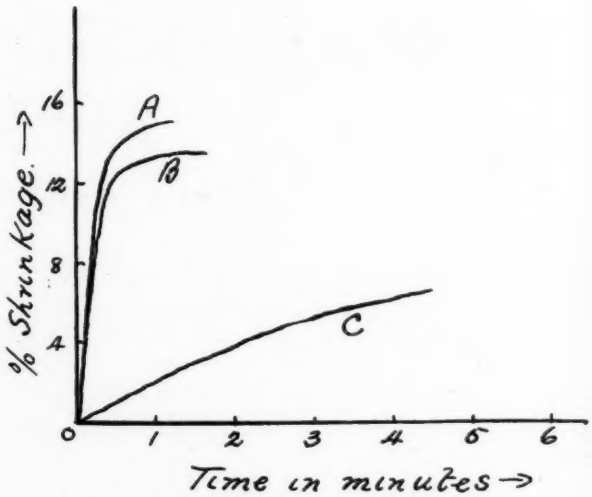

Fig. 1.—Curves showing amount of shrinkage with and without 1% Mercerol in caustic soda of 53° Tw.
A—Grey cotton yarn (with Mercerol)
B—Desized cotton yarn (with Mercerol)
C—Grey cotton yarns (without Mercerol)

Later it was found (E. P. 359399) that the hydrogenated aromatic compounds could be dispensed with altogether, and in their place could be used various ether derivatives of polyhydric aliphatic alcohols containing at least one hydroxyl group. Suitable derivatives are the mono-alkyl or aryl ethers of glycol and polyethylene glycols, the polyethylene glycols themselves, and the acetals of glycerine. In general the phenol content of the mixture should be between 60 and 98%. Two examples are—

(1) 85% of Phenol
15% of Di-ethylene glycol mono-ethyl ether

(2) 92% of Commercial xylenol mixture
8% of Di-ethylene glycol mono-dibutyl ether

and as with most of the wetting-out agents of this type only about 1% addition to the mercerizing liquor is required.

Phenol is of course practically non-volatile and therefore does not evaporate from a mercerizing liquor. It is important that the second component (added for the purpose of increasing the somewhat low wetting-out power of the phenol itself) should be equally non-volatile. Aliphatic alcohols are of course liable to evaporate slowly, especially those of low molecular weight. This principle

underlies the wetting-out agents described in E. P. 360472 in which phenol is retained as the main component as hitherto, but the hydrogenated aromatic compounds are replaced by certain polyhydric aliphatic and aryl-aliphatic alcohols which contain at least one carbon atom more than the number of hydroxyl groups. These products may be obtained by oxidation of olefine hydrocarbons other than ethylene, and also by reduction of ketones (these products are usually known as pinacones). Wetting-out agents of this type have excellent stability and an example is the following:

85% of commercial cresol mixture
15% of Pinacone (tetra-methyl ethylene glycol).

The wetting-out agent should in general contain not less than 60% of phenol or its equivalent.

A wider range of the substances mentioned in E. P. 359399 is claimed in a later patent (E. P. 361865). Apparently it is very satisfactory to use mixtures of phenol with saturated or unsaturated mono- or polyhydric alcohols of the aliphatic, aryl-aliphatic, hydro-aromatic, or alicylic series which contain at least one carbon atom more than the number of hydroxyl groups, or with ketone alcohols and such ethers of polyhydric aliphatic alcohols which contain at least one free aliphatic hydroxyl group.

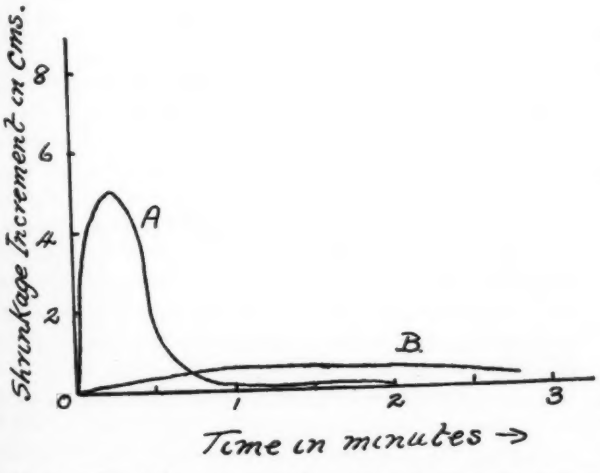

Fig. 2.—Curves showing rate of shrinkage with and without 1% Mercerol in caustic soda of 53° Tw.

A—With Mercerol
B—Without Mercerol

A new line of progress was indicated in E. P. 364844 in which claim is made for the use of phenol mixtures with certain nitrogen-containing substances. Instead of the hydrogenated aromatic compounds it was found possible to use certain primary, secondary, tertiary amino and also quaternary ammonium compounds; a number of the derivatives of these compounds were also proved to be useful. Even hydrazines and heterocyclic bases were utilized. Thus claim was made for the use of such substances as benzylamine, aniline, phenyl hydrazine, pyridine, and phenyl-trimethyl-ammonium-methyl sulfate.

Quite interesting is the fact that neither the phenol nor the nitrogen compound have wetting-out powers equal to those of the mixtures of these substances.

Typical wetting-out agents having a composition of this nature are:

(1) 80% of commercial cresol mixture
20% of tri-ethanolamine —— $N(CH_2CH_2OH)_3$

(2) 70% of commercial cresol mixture
30% of pyridine

In general it is desirable that all the components of the wetting-out agent should be completely soluble in caustic soda of mercerizing strength. It will be remembered that this condition debars the use of soap products such as Turkey red oil and Marseilles soap; such substances are apparently salted-out by the caustic soda and form an insoluble scum. The discovery has been made however that phenol has a solubilizing action on certain compounds which are normally insoluble in strong caustic soda, and this phenomenon makes possible their use. For example, camphor is quite insoluble in a mercerizing liquor, but in the presence of phenol it can be employed and incidentally confers good penetrating power on the liquor. New wetting-out mixtures based on this discovery are described in E. P. 365323.

Wetting-out agents of this type consist of phenol and up to 40% of camphor or commercial acetone oils (these are produced by the method described in U. S. P. 1656488, in which sugars are subjected to a butyric fermentation in the presence of calcium carbonate, a commercial product being known as Ketol). Examples of these newer wetting-out agents are:

(1) 92% of Commercial cresol mixture
8% of camphor

(2) 75% of Commercial cresol mixture
25% of Ketol

At this stage it may be useful to give some idea of the stability of mercerizing liquors containing added wetting-out agents, especially those of the types dealt with above. K. Bauer and H. Brandenburger (Textilber., 1931, *12*, 336) have recorded the behavior of caustic soda solutions containing 1.5% of Mercerol when stored over various periods up to 30 days, and their results are as follows:

Time after immersion of cotton yarn	*Per cent shrinkage of yarn in mercerizing liquor after storage for:*				
	Immediately	*1 Day*	*3 Days*	*6 Days*	*30 Days*
10 seconds	0.5	1.2	10.6	3.1	10.4
20	3.1	4.7	19.6	10.0	19.4
30	7.4	9.7	23.9	18.2	23.2
60	20.7	24.1	27.6	27.7	27.2
1½ minutes	27.8	28.5	28.3	28.9	28.0
2	28.9	29.1	28.9	29.2	28.3
3	29.6	29.5	29.4	29.6	29.0
5	30.0	30.0	30.0	30.0	30.0

The interesting point revealed by these results is that the shrinking power of the mercerizing liquor actually increases during storage up to about three days. It is difficult to explain this behavior unless it can be perhaps

traced to an oxidation effect, it being known that sodium phenate is susceptible to changes of this nature. The essential feature, however, is that the shrinking power does not decrease with standing.

Apparently the penetrating power of a mercerizing liquor must not be confused with its shrinking power. This point is emphasized by some further measurements of Bauer and Brandenburger in which the penetrating powers of caustic soda solutions containing 1.5% of Mercerol were measured after various periods of storage by noting the times of sinking of similar pieces of cotton woven fabric. These results are as follows:

Period of storage of mercerizing liquor	*Time of sinking of fabric*
Immediately	13.4 seconds
1 day	15.6
3	16.7
6	10.5
30	12.7

Again an increase of penetrative power is noticed up to the third day but this increase is very small and not nearly so important as the shrinking power previously noted.

Returning to the composition of wetting-out agents it may be noted that recent developments include the use of mixtures of phenols with substituted diamines (E. P. 368606) such as mono-oleyl-ethylene diamine and mono-oleyl diethyl ethylene diamine. These mixtures contain at least 60% of phenol and a typical product is:

90% of commercial cresol mixture
10% of di-ethylamino-ethyl-oleylamide

Di-ethylamino-ethyl-oleylamide has the following composition:

$CH_3(CH_2)_7CH=CH(CH_2)_7CONHCH_2CH_2N(C_2H_5)_2$

Certain alicyclic carboxylic acids have also been found to have a beneficial effect when added to phenol mixtures and they may therefore be employed to replace the hydrogenated aromatic compounds at first found suitable for this purpose (E. P. 279784). The carboxylic acids most satisfactory are those known as naphthenic acids (E. P. 378194) and which are obtained from natural oils or petroleum residues; also colophenic, abietic, and pimaric acids derived from natural resins may be employed. Typical wetting-out agents of this type are as follows:

(1) 80% of commercial xylenol mixture
20% of purified commercial naphthenic acid

(2) 80% of chlorphenol
20% of purified commercial naphthenic acid

The use of naphthenic alcohols instead of the acids is claimed in E. P. 394499, and this patent also contains some interesting information concerning the stability of wetting-out agents of this type. It will be remembered that in earlier patents dealing with wetting-out agents for mercerizing liquors, the products described consisted of mixtures of phenol with hydrogenated aromatic compounds (E. P. 279784) such as cyclohexanol, and also with aliphatic and aryl alcohols (E. P. 350018) such as *n*-butyl and benzyl alcohols. Apparently these mixtures are considerably less stable (when added to a mercerizing liquor) than those prepared with a naphthenic alcohol. The following results, obtained by noting the times of sinking of pieces of grey cotton fabric in mercerizing liquors stored for various periods, illustrate this point. (See table below).

The above data was obtained with liquors produced by adding 2½ parts of the wetting-out agent to 100 parts of caustic soda of 55° Tw. It is obvious that the wetting-out power of the naphthenic alcohol is superior to that of the corresponding acid (the alcohols are obtained by reduction of naphthenic acids) and also to that of such substances as benzyl and *n*-butyl alcohol. Glycerine is evidently quite useless as an addition to a mercerizing liquor for the purpose of improving its penetrative properties.

Not all wetting-out agents for mercerizing liquors have phenol as a chief constituent. I. G. Farbenindustrie A.-G. have found (E. P. 354946) that the sulfuric acid esters of certain low molecular weight aliphatic alcohols are useful wetting-out agents. This is somewhat surprising, since in ordinary neutral or weak acid and alkaline liquors these substances have quite small surface tension reducing properties. Apparently it is only in strong alkaline solutions that they act as efficient wetting-out agents. Products of this composition are produced by the action of chlorsulfonic acid on the alcohol dissolved in an inert organic solvent. In using them for mercerizing liquors it is preferable to mix them with a small amount of a water-soluble hydroxyl compound such as glycerine, ethyl alcohol, and 1:3-butylene glycol monoethyl ether since this renders them more soluble in the mercerizing liquor. The following is an example of the composition of a wetting-out agent of this type:

85% of the sulfuric acid ester of *n*-amyl alcohol
15% of 1.3-butylene glycol mono-ethyl ether.

(Continued on page 628)

Composition of wetting-out agent	*Time of sinking in mercerizing liquor after:*		
	1 *day*	2 *days*	3 *days*
9 parts of cresol + 1 part of *n*-butyl alcohol	3 secs.	3–4 hrs.	.....
9 parts of cresol + 1 part of glycerine	5–6 hrs.	.....	.....
9 parts of cresol + 1 part of benzyl alcohol	130 secs.	200 secs.	300 secs.
9 parts of cresol + 1 part of cyclohexanol	3 secs.	4–5 secs.	70 secs.
9 parts of cresol + 1 part of naphthene alcohol	3 secs.	4–5 secs.	7 secs.
9 parts of cresol + 1 part of naphthenic acid	60 secs.	106 secs.	117 secs.

Rayon Dyeing and Finishing-15

By **B. L. HATHORNE**
Consulting Textile Chemist

CHAPTER III—SOME PHYSICAL ASPECTS OF REGENERATED CELLULOSE RAYON DYEING

(Continued from page 556, Sept. 11th issue)

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So many theories regarding the dyeing of vegetable and synthetic fibers have been advanced, that we will not further complicate the situation by adding another theory to the confusion already current. We will confine ourselves to observed facts.

When regenerated cellulose rayons are first immersed into dye liquors, particularly, if there is salt present, an appreciable quantity of dyestuff attaches itself to the outside of the individual filaments. Microscopic cross sectional examination of dyed filaments proves this beyond the shadow of doubt. It is evident that there must be some affinity between the fiber and the dyestuff:—otherwise the dyestuff would remain in solution or would precipitate as readily upon the walls of the dye vessel as it does upon the surface of the individual rayon filaments.

As the temperature of the dye bath is raised, the dyestuff particles gradually become dispersed throughout the filaments being dyed. The progress of this dispersion of dye particles can easily be followed by means of microscopic examination. If the dyeing operation is continued long enough at an elevated temperature each individual filament becomes uniformly dispersed with dyestuff throughout its entire cross section. Although individual filaments become uniformly colored by a long continued dyeing treatment at an elevated temperature when the so-called poor levelling colors are used, the noticeable variations in depth of shade from filament to filament are not overcome even when an unusually long period of processing is resorted to. This is concrete evidence of a variation in the physical structure of individual rayon filaments.

Again we wish to point out that there must be some force of attraction between the dyestuffs that dye rayon and the fiber. It is very apparent that dyestuff particles cannot easily migrate to the center of rayon filaments. There must be some force of attraction that draws or pulls dyestuff particles to all parts of the filaments and holds them firmly in place. It is obvious unless such a force is present dyestuff particles would remain in solution or suspension or would penetrate rayon filaments only partially.

When two rayon filaments, manufactured from the same batch of spinning solution, but which have been stretched varying degrees during the spinning operation, are dyed simultaneously with a dyestuff of known uneven dyeing properties, the following phenomena are observed:

(1) The rayon stretched to the lesser degree during spinning dyes more rapidly and deeply than does the rayon to which the greater amount of stretch has been applied.

(2) As the temperature of the dye bath is raised, the two filaments become more nearly uniform.

(3) When the two fibers are held at or near the boil for a long period of time, they are dyed more uniformly than is the case when they are dyed for a lesser period of time, or at a lower temperature.

(4) The use of a precipitating agent of any kind (Glauber's Salt, common salt, etc.) causes the difference in depth of shade between the two yarns to be materially increased provided that the salt is added at the same rate at which it must be added in commercial dyeing procedures.

(5) The use of salt in the dyeing operation checks or retards the levelling action (from skein to skein) of a boiling dye bath.

(6) The use of a retarding agent such as soap or soluble oil aids somewhat in producing a more uniform shade between two fibers.

Tension applied to regenerated cellulose rayons during the dyeing operation retards dyestuff penetration of the great bulk of all substantive dyestuffs although this retarding effect is not uniformly pronounced for all dyestuffs.

Uneven tensions applied to rayon yarns during fabric manufacturing processes (spooling, beaming, warping, weaving, etc.) can seriously effect the level dyeing properties of the particular rayon treated, particularly when the treated fabrics are dyed in such a manner that uneven tensions existing in the fabric must be maintained throughout the dyeing operation.

Strong alkaline treatments, for example, a short treat-

ment with a caustic soda solution, improve the dyeing properties of uneven dyeing rayons. This treatment has been found the most effective of all the various "cure alls" that have been offered to the practical dyer. When the nature of the fabric and the machinery available for handling the same is such that it is feasible, a strong alkaline treatment before dyeing materially improves the dyeing results obtained on any regenerated cellulose rayon fabric.

Unfortunately the strong alkaline treatment described above detracts slightly from the strength of the treated fabric.

The commonly used bleaching and stripping agents such as sodium hypochlorite, peroxide, permanganate, hydrosulfite, etc., cause rayons of uneven dyeing properties to dye more nearly uniform. It has been estimated that each of these materials used singly, will improve the dyeing properties of uneven dyeing rayon approximately twenty percent. Unfortunately, the effect is not cumulative.

WETTING-OUT AGENTS

(Continued from page 626)

Finally, in concluding this record of progress in rendering mercerization more efficient, mention must be made of the new wetting-out agent (Shirlacrol) introduced by the British Cotton Industry Research Association. This product is protected by E. P. 390824 and consists of a selected portion of the tars acids obtained from coal tar distillates. It is very cheap and effective. Most probably it consists largely of phenol, and particularly cresylic acid residues, and is therefore related to many of the products described above. It is completely soluble in the mercerizing liquor, although insoluble in water, and it is claimed that it gives mercerizing liquors a penetrative power equal to that obtained with any other available product.

CULTIVATING OUR DYES TRADE IN LATIN AMERICA

By Alfred Thomas Marks

UNITED STATES dyestuffs exporters have a remarkably potential sales field in the Latin-American countries to the south. In the more prosperous years from 1925 to 1930 these exports from the United States averaged from $750,000 to close to one million dollars annually—until the coming of depressed economic conditions served to decrease the volume of the trade and reduce the demand. However, recent reports from the more progressive of the countries indicate a substantial revival of these exports with steadily increasing shipments.

The significant fact to keep in mind in considering these nearby markets is that a very large percentage of these exports are used for the manufacture of textiles, the Spanish Americans being extremely partial to color in wearing apparel, decorative fabrics for the home and for all other purposes.

In order that we may better "size up" this trade it is advisable that we glance briefly at the larger individual markets in South and Central America. This will give us a better working knowledge or just where we may most profitably direct our efforts for the winning of the business. We find, upon carefully surveying our dyes exports to the nations under discussion, that our seven best and most promising markets are, in the order named, Argentina, Mexico, Cuba, Chile, Brazil, Colombia and Peru. As indicating the reawakened demand for American dyes in these countries the Department of Commerce reports having very recently received many requests from importers there for information which will enable the writers to get in touch with our United States manufacturers in order to either make direct purchases or secure agencies. Among these are the following:

A well known firm of importers located in Mexico City, Mexico, will arrange to make regular purchases of aniline dyes. Will also accept an agency for that country. (Inquiry No. 5050.)

Purchases of American textile dyes will be made by a leading firm located in La Paz, Bolivia, South America. (Inquiry No. 5076)

A firm located in Rio de Janeiro, Brazil, South America, will make direct purchases of materials for the manufacture of textile dyes. (Inquiry No. 4860)

A prominent chemical firm located in Buenos Aires, Argentina, South America, will arrange to make regular purchases of materials and machinery for manufacturing textile dyes. An agency can also be placed. (Inquiry No. 4814)

American textile dyes, anilines, etc., are wanted by a well known firm of importers located in Mexico City, Mexico. This concern will make direct purchases and also take an agency. (Inquiry No. 4672)

Machinery and equipment for making textile dyes are wanted by a firm located in Valparaiso, Chile, South America. Purchases will be made for cash and an agency can be arranged. (Inquiry No. 4734).

Dyes suitable for coloring straw hats for women and children are wanted by a widely-known firm located in Curacao, Netherland West Indies. This firm will make direct purchases. (Inquiry No. 4603)

American textile dyes are wanted by a leading firm of importers located in Barranquilla, Colombia, South America. All purchases will be made for cash and an agency can be arranged. (Inquriy No. 4615))

Full lines of textile dyeing materials are wanted by a leading firm located in Rio de Janeiro, Brazil, South America. Will purchase for cash and also take an agency. (Inquiry No. 4507)

(Continued on page 645)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

OCTOBER 23, 1933

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CALENDAR OF COMING EVENTS

Meeting, New York Section, Elm Golf Club, Paterson, N. J., October 27.

* * *

Fall Meeting, Southeastern Section, Ralston Hotel, Columbus, Ga., October 28. Members from other Sections are requested to send reservations to C. B. Ordway, Secretary, Southeastern section, if they wish to attend.

* * *

Annual Meeting, National Association, New York City, December 8.

THIRTEENTH ANNUAL CONVENTION

Saturday Afternoon Session

On the following pages will be found several of the papers presented at the Saturday afternoon session of the Annual convention held in Chicago. The remainder of the papers presented at this session are not yet ready for publication but will be published in the near future.

UNEMPLOYMENT REGISTER

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive

NOTE. Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the AMERICAN DYESTUFF REPORTER.

A-2

Education—B.T.C., Lowell Textile Institute, 1932; also course in shorthand and typing.

Experience—None to date, interested in quantitative analysis, experimental dyeing, color matching, dye testing and dye identification. Ability to learn quickly and will go anywhere. 23 years old, single.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-E-2

Education—B.T.C., Lowell Textile Institute, 1933.

Experience—Assistant instructor in chemistry, Lowell Textile Institute. Member of scholastic honorary fraternity.

(Continued on page 637)

Proceedings of the American Association of Textile Chemists and Colorists

Chemical Constitution and Wetting Action*

By **W. KRITCHEVSKY**
Rit Products Corp.

THE wetting out properties of certain organic chemicals have a definite relationship to their chemical constitutions, and definite groupings present in those chemicals are responsible for their wetting out action.

The interfacial tension of a solid against a pure liquid is important for the phenomena of wetting and of displacement of one liquid by another, and those phenomena are largely similar to the phenomena of spreading of an oil on the liquid with the difference that in place of one of the liquids we have a solid, and the values obtained in the study of the spreading of oils on liquids can be properly used for the explanation of the wetting out of solids by liquids.

Two American scientists, Dr. W. D. Harkins and Dr. Irving Langmuir, have independently and through different lines of reasoning studied the properties of surface films on liquids which studies explain wetting out action both from physical and chemical standpoints.

They have proven that certain organic chemicals like most of the hydrocarbons will not spread on the surface of water, oleic acid will spread in a very thin layer all over the surface of the water. What is true of oleic acid is also true of any organic chemical having a carboxyl group, a hydroxy group, an amino group, a $CONH_2$ group, etc. They call those groups, as enumerated just above, "polar" groups or "active" groups while the hydrocarbon chain linked to them they call "non-polar" or "inactive" groups.

When a chemical having both polar and non-polar groups like oleic acid is spread on water the polar group dips into the water, being soluble in it, the non-polar group is above the water surface.

The film of any liquid in contact with water is composed of molecules oriented so that the active (or polar) group at the end of any hydrocarbon chain is in contact with the water. The double bond of an unsaturated hydrocarbon, and the double bonds in the benzene ring, act in this respect like polar groups.

The introduction of a polar group at the end of even a very long hydrocarbon chain increases greatly the attraction for water and that attraction is very nearly independent of the length of the chain. This indicates that at all such interfaces the active group must be turned toward, and practically in contact with, the water.

Harkins and Feldman get to the root of the matter by considering the factors involved in the spreading of liquids over the surface of water. They figure that the polar group or the active group does the work of adhesion of the oil to the water, as acting against it is the work of cohesion of the oil itself. If we should express the work of adhesion of the polar group to water by Wa and the work of cohesion by Wc then the spread of the liquid of the oil on water could be expressed by the equation: $S = Wa - Wc$. In other words, the decrease of free energy on spreading is numerically equal to the difference between these two quantities.

Dr. Harkins and Feldman have determined the spreading values for a number of chemicals and I believe that if the same determination should be applied to the present wetting agents it may give us the numerical values for the efficiency of wetting agents.

Taking the above into consideration it is evident that both the solubility and the wetting out action of organic compounds depend entirely upon the equation of $S = Wa - Wc$. Considering, for instance, a fatty acid of the general formula R-CCOH in which R is the hydrocarbon chain and the -COOH is the polar group—then it is evident that if the R is short then the work of the -COOH is greater; in other words, Wa is greater than Wc, while if the R represents a long chain then the difference becomes smaller. In other words fatty acids, and the same is true to alcohols, amines, amides, etc., with short hydrocarbon chains z are practically soluble in water, and as the length of the chain increases the solubility decreases, while on the other hand all of them will spread upon water. From this Harkins concludes that the adhesion of an organic chemical to water is determined by the active group while the solubility depends on the whole molecule.

The free energy decrease, when the surface of an oil approaches that of water (a polar liquid), depends primarily upon the most active or polar group present in

*Presented at Saturday afternoon session, Annual Convention, Chicago, Sept. 9.

the molecule, and in a secondary way upon the shape and size of the molecule.

The polar group to be most active must be at the end of a molecule as it is the one directed downwards; for instance, while palmitic acid will spread upon water because the COOH group is at the end of the molecule, yet as N. K. Adams has proven, benzyl palmitate or palmitic anilide do not form films simply because the polar group is prevented from approaching the water closely enough.

According to this line of reasoning the decrease of free energy when ester comes in contact with water is less than the corresponding value for the acid.

In accordance with the previous discussion, it is evident that the spreading action as well as the wetting action is a function of the decrease of potential energy when two liquids get together, and Dr. Irving Langmuir has supplied a very workable formula that can also be applied to the modern wetting agents which will indirectly determine their efficiency as such.

According to his formula the decrease of the potential energy λ when a mol passes from the interior to the surface of the solution equals $\lambda = \lambda o + 625_n$, λo being the constant for each homologous series depending on the nature of the end group and $_n$ = the number of carbon atoms in the molecule.

The values of λo were:

	Values of λo
Teritary alcohol	950
Primary amine	600
Primary alcohol	575
Ester	470
Monobasic acid	437
Ketone	295
Aldehyde	210
Amide	—510
Dibasic acid or alcohol	—700

A double bond in the molecule decreases λo by about 400 and every additional hydroxyl group in an acid decreases it by about 800.

λ being the decrease of a potential energy when a mol passes from the interior to the surface naturally the small value indicates high polarity or a tendency to dissolve in water, the smaller the λ is the bigger the spreading power, the greater the emulsification value, and as a rule the greater the wetting action. According to his table it is evident that wetting agents form a dibasic acid or alcohol, a -CHOH-CH_2OH would make the best wetting agent provided the rest of the chain is of equal length and arrangement. The amides would come next and so on, provided the $_n$ is equal.

Now after this brief theoretical foundation for the evaluation of wetting agents and determining their relation to the chemical constitution, we shall pass over to practical considerations.

From the above said, it is evident that any chemical having a polar and non-polar group will be soluble in water if the non-polar group is short, and the polar group being very strong in relation to the non-polar group.

Chemicals like this have been investigated by Dr. Carl Neuberg in 1916 and he named them "hydrotropes." Hydrotropes are chemicals that when dissolved in water in certain concentration will dissolve chemicals insoluble in water in their particular solution. Dr. Neuberg's work I would consider as the first introduction into the knowledge of wetting out action.

While hydrotropes could be considered as extreme wetting out agents in principle, in many cases they are not good emulsifying agents by themselves or even wetting out agents as will be explained later.

As antithesis to hydrotropes that have powerful polar groups and weak non-polar groups come long chain fatty acids, alcohols, amides and similar derivatives that have very long hydrocarbon chains or non-polar groups, and the same type of polar groups as previously mentioned. In these cases the attraction for an oil layer will be greater than for the water layer and while those compounds will spread—they will not form a very good wetting out agent in an aqueous medium, although they may be excellent wetting out agents in an oil medium like lubricating oils, etc.

In contra-distinction to hydrotropes, meaning chemicals that are attracted to water, we may call these chemicals lipotropes; viz., chemicals that are attracted to oil. Another nomenclature that would be very apt in this case would be one designed by B. R. Harris in his latest series of patents (and afterwards the same nomenclature was found in the German literature) in which the lipotropes are called "lipophiles" and the hydrotropes, of course, the well known definition "hydrophiles." As mention before, neither the hydrotropes nor lipotropes are ideal wetting out agents because in one case they show too much preference to water and in the other case too much preference to oil, while in order to have a good wetting out agent, it seems that there must be a certain balanced ratio; in other words, the lipophilic character must be pronounced and, as practical experience shows, some of the best wetting out agents must have a carbon chain of at least 8 carbon atoms and don't reach their maximum efficiency until 12 carbon atoms are in the chain. I might mention in passing that if there are more than 18 carbon atoms in the chain the wetting out efficiency goes down again.

On the other hand, the hydrophilic group is not sufficiently strong enough to lend lipophiles of the kind just mentioned enough adhesion to the water layer and for this reason the hydrophilic group must be fortified by additional hydrophilic groups as the modern wetting agents indicate.

Here is where it is evident that there is a great analogy between the relation of color of dyestuffs to their chemical

constitution and the relation of wetting action to the chemical constitution of wetting agents.

I am referring to the well known theory of Otto Witt. Otto Witt has established that every dyestuff must have a chromophoric group; in other words, a group that bears the color and also an auxochromic group, a group that assists in bringing out the color. For instance azo benzol:

$$C_6H_5 - N = N - C_6H_5$$

having a chromophore $-N = N-$ is colored but not strong enough to be a dyestuff. On the other hand, if a salt forming group is added to it, like an amino group or a hydroxy group, then the colored compound becomes a dyestuff. In this case it would mean

$$C_6H_5 - N = N - C_6H_4 - OH$$

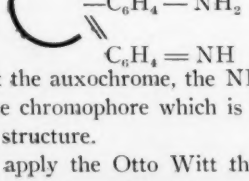
or

$$C_6H_5 - N = N - C_6H_4 - NH_2$$

Those compounds again are dyestuffs, but yet they are not water soluble. In order to become water soluble the amino group should have an acid added to it while the dyestuff which has a hydroxy group, an alkali and both of them have to be sulfonated and have a sulfonic acid group which makes them water soluble.

The sulfonic acid group not only helps the solubility but it also acts as a semi-auxochrome as it is proven that it shifts the color a few shades and also increases the fastness in many cases.

I have observed that the auxochromes and semi-auxochromes come either in direct contact with the chromophore as in chinonimine dyes or removed from the chromophore as in azo dyes. When the auxochrome and semi-auxochrome are directly attached to the chromophore the color strength of the dye is greater than otherwise, and it is evident basic dyes have a greater color strength than azo dyes; for instance on taking para-roseaniline formula given below:



it is clear that the auxochrome, the NH group, is directly attached to the chromophore which is the double bond of the chinoidal structure.

Should we apply the Otto Witt theory and my additional observations to wetting out agents—I believe it will be clear that the same theory can be modified and applied to wetting out agents.

While fatty alcohols having a chain of above C_8 (same is true to fatty acids, amides and so on), spread on water and have a polar group and act as wetting agents in non-aqueous media—yet are not much wetting agents in water, as their hydrophilic group is not strong enough. On the other hand, if this hydrophilic group is fortified with additional hydrophilic groupings as you will see from the following formulas they become very powerful wetting agents.

For the sake of analogy, we shall call the lipophilic groups "lipophores," the hydrophilic groups "hydrophores" and the fortifying groups "auxohydrophores." This gives us a definite nomenclature that will enable us to clearly discuss the effect of those groups and their wetting out properties.

I am giving below a table of a number of wetting agents—some of them are commercial, some of them are in the semi-commercial process. They are all patented and described in the literature. For this reason I am not naming any of them by their commercial name and just giving the chemical formula and the prototypes of each one of them.

Commercial and Semi-Commercial Wetting Agents

Derived from $R - CH_2OH$

1. $R - CH_2 - O - SO_3X$ $X =$ metal

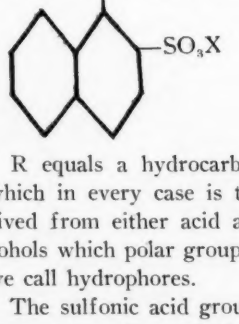
Derived from $R - COOH$ and $R - COO - R'$

2. $R - CO - O - CH_2 - CH_2 - SO_3X$
3. $R - CO - O - CH_2 - CH_2 - O - SO_3X$

Derived from $R - CONH_2$

4. $R - CO - NH - CH_2 - CH_2 - SO_3X$
5. $R - CO - NH - CH_2 - CH_2 - O - SO_3X$
6. $R - CO - NH - CH_2 - CH_2 - NR_2'' -$ $(R'' = CH_3, C_2H_5)$

Derived from a Cyclic Hydrocarbon

7. 

R equals a hydrocarbon chain, say from C_{10} to C_{18} which in every case is the lipophore. They are all derived from either acid amides, esters, fatty acids or alcohols which polar groups or the radicals of those groups we call hydrophores.

The sulfonic acid groups or other salt forming groups present we call auxohydrophores.

According to the previous discussion, it is clear that those derived from the amido group should be better wetting agents than those derived from any other group, provided everything else is equal. Those having double bond in the lipophoric group would be strong wetting out agents, and yet I don't believe the field is by any means exhausted, as according to the theories above, wetting agents derived from a di-carboxyl group, di-hydroxy group or hydroxy-carboxy group should be the stronger yet. Those considerations cannot be applied exactly for the commercial wetting agents as none of them are in a commercial pure state and they are all cut and diluted up to certain strengths.

Then again there are certain things to be explained, for instance, in formula No. 6 given above, the commercial wetting agents represented are attributed in the litera-

ture to wet out at the rate of 1 to 50,000 while my experience did not confirm it.

From the above considerations it is evident also that one is enabled to pick wetting agents or emulsifying agents or finishing agents from this group to suit his demands.

If wetting alone is required a lipophore, having a group of about C_{12} would be just the type required. If finishing or oiling is required, a lipophore around C_{16} to C_{18} would be the best.

On the other hand, a wetting out agent having $R = C_{18}$ but having a double bond in the lipophoric group like in the case of oleic acid will be a better wetting agent than one having the same number of carbon atoms but not having the double bond like stearic acid.

I believe that in these short remarks I have practically said what I wanted to say. If there are any questions, I shall be glad to answer them.

Discussion

Chairman Cady: Is there any discussion of this paper?

Mr. Schroeder: I should like to ask where pine oil is on that chart?

Dr. Kritchevsky: I don't think pine oil is much of a wetting agent. As a matter of fact, I didn't mention pine oil or sulfonated oil. The reason I didn't is that for instance in sulfonated oils the assistant wetting agent, the auxohydrophore, is not at the end of the lipophoric chain but in the middle, and it is so included that it cannot approach the water phase. For that reason it is not a good wetting agent. While pine oil may have its technical uses for certain things it isn't in line with any of these wetting out agents. A few years ago it might have been considered all right. That doesn't mean it hasn't some application, but it means that in this case where we are speaking purely about the relation of chemical constitution to wetting out action, I naturally brought out the extreme cases.

Dr. Carl Z. Draves: You bring out your theory more particularly with respect to soap, sodium oleate, for instance.

Dr. Kritchevsky: Sodium oleate, while it spreads and has wetting out action, and while it does have COOH and while it also has a little assistance from double bond, it doesn't have an auxohydrophore group. In other words, there is nothing in it to fortify the action of this in order to make it work as a good wetting out agent. Take this and substitute the oleic acid with any one of above given wetting agents derived from oleic acid and you will get a very good wetting agent, and there are commercial wetting out agents that are made from oleic acid in this way. Soaps are good wetting agents, to a certain extent, but we are not talking qualitatively now, we are talking quantitatively. We have to assume the term "wetting agent" to mean not just simply any compound that will wet out but any compound that will wet in a concentration of 1 to 1000 in a minimum amount of time.

Member: Is there any good wetting agent that is also a good penetrating agent?

Dr. Kritchevsky: Yes. Wetting, penetrating and emulsifying go together, except that one that may be a good emulsifying agent will not be a good wetting agent if the lypophoric group is too short. Those that balance in a certain proportion, beginning with C_8 will make good wetting agents.

Mr. Schroeder: Won't a rising temperature of the water alter the range?

Dr. Kritchevsky: Well, I will be frank with you and say that I haven't studied that. In general I would say that it does. When you have to work out something, you must work under standard conditions, standard conditions in an ordinary plant. A rising temperature will naturally help wetting out quite a bit and that applies in the case of wetting agents with longer lipophores.

Mr. Epstein: I believe Dr. Kritchevsky should be complimented for endeavoring to bring a little order into the chaos that exists in the chemistry of wetting agents. I want to call his attention to a recent paper by Dr. Clayton in "The Chemical Manufacturer" of 1932, in which he discusses the theory advanced in Harris' patents, and he points out that in connection with emulsifiers and wetting agents, besides the factor of interfacial tension and the factor of adhesion, there are other factors, such as the orientation, or the structure of the molecules of the liquid, which is a very important factor.

He refers to a paper by Spielman and Chamberlain from the Leeds Textile School of London in which they point out that, for instance, oleic acid or oleol alcohol added to a wool is difficult to wash out with soap and soda; that if the wool is added, let us say, with paraffin oil, it is much easier to wash out, although oleol alcohol has a much lower interfacial surface tension than straight hydrocarbon paraffin oil. If, however, you add the oleol alcohol to the paraffin oil in a certain percentage, like six per cent, the amount of oil left after washing it out is very small. And they show there that it is due to certain orientation or cubical structure of the molecules in the liquid.

This is another contribution in this connection which perhaps may help to explain why certain wetting agents do work and some don't, in addition to the important points brought out by Dr. Kritchevsky.

Dr. Kritchevsky: I should like to say that while what you say may be true—and I don't doubt that it is—I did not discuss in this paper anything outside of the factors involved in the wetting agents themselves; I did not discuss the intermediaries. That would bring in so many more questions that we couldn't discuss it today within the short time allotted and yet it would not change the character of this discussion. For that matter, I have

omitted quite a number of other theories as, for instance, those brought out by N. K. Adams which enable us to express the activity of polar groups in terms of square Angstrom units and a lot of other work in connection with this subject, because they would not change the conclusions arrived at, and besides, as I say, we cannot be guided by too many factors in determining something. There is no doubt as I say that what you say has quite a bearing on the subject.

Chairman Cady: I am sorry to have to interrupt this interesting discussion but our time is limited and we must continue with our program.

Our next speaker will be Lloyd W. Davis, of the National Oil Products Company, who will speak on the subject, "Modern Theories of Sulfonated Oil."

. . . Mr. Davis presented his prepared paper . . . (Applause.)

Modern Theories of Sulfonated Oils*

By **LLOYD W. DAVIS**

Chemist, Technical Service Dept., National Oil Products Co., Inc.

SULFONATED oils have been known and used for a long time in almost every type of industry. However, this afternoon let us confine our remarks to those which are applicable to the textile industry.

Although you are all probably familiar with sulfonated oils or fats, let us try to clear up a few points before discussing these products.

The question has been asked many times, "What are sulfonated oils?" In answer we may say that in general they are not sulfonated at all, but are really the half sulfuric acid esters of fatty acids or glycerides neutralized with some base to form the corresponding alkali salt.

A second question frequently asked is, "Why are oils sulfonated?" The answer here is that oils or fatty materials exhibit properties which make them desirable for use in the textile industry. Furthermore, it is often desirable to apply these materials in the form of aqueous emulsions and sulfonation is one of the best methods for rendering fats and oils emulsifiable in water. In addition certain sulfonated oils have decided emulsifying properties and may therefore be used to disperse raw oils or other materials in water. Certain other types of sulfonated oils have the ability to lower the interfacial surface tension between water and textile fibers. Consequently, they are used as wetting out and penetrating agents.

Let us examine the materials which may be used in sulfonation and the chemistry involved. Until quite recently only natural fats, glycerides or fatty acids, were used to produce sulfonated oils. Of these only those containing ethylene linkages (double bonds) or hydroxyl (OH) groups could be used. A still further limitation excludes the highly unsaturated fats, such as linseed oil or fish oils, because the yoxidize and polymerize so readily to dark colored viscous compounds as to be dangerous for use on textiles. The most common fats used for sulfonation are castor oil, which contains both an hydroxyl group and an ethylene linkage, olive oil and tallow which contain only double bonds.

The sulfonating agents used are sulfuric acid of various strengths; fuming sulfuric acid or oleum, which is concentrated sulfuric acid containing certain percentages of dissolved sulfur trioxide; chlorosulfonic acid, which is sulfuric acid with one hydroxyl group replaced by chlorine; and sulfur trioxide itself.

The actual formation of the sulfuric acid ester is carried out either by direct addition at the ethylene linkage of the fat with consequent saturation or by reaction between the sulfonating agent and the hydroxyl group of the fat with the formation of water or where chlorosulfonic acid is used, the formation of hydrogen chloride (HCl).

This all seems very simple—just permit equivalent portions of the fat and the sulfonating agent to react under the proper conditions and an equivalent amount of the ester is formed. However, chemical reactions in general are never as simple as they first appear. In this case the law of mass action plays an important part. Because no product is removed from the field of action, the desired reaction does not run to completion, but approaches an equilibrium where the rate of decomposition equals the rate of combination. This equilibrium may be displaced

*Presented at Saturday afternoon session, Annual Convention, Chicago, Sept. 9.

within limits by varying the ratio of the reacting substances.

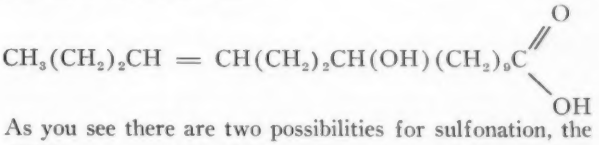
It might be well to state here that the reactions just mentioned are not the only ones which take place when fats or oils are sulfonated. There are many troublesome side reactions which occur at the same time. Some of these are: hydrolysis of the glycerides with the formation of free fatty acid, polymerization, oxidation of the fat and reduction of the sulfonating agent, and hydrolysis of the acid ester accompanied by the formation of saturated hydroxy fatty acids. Thus it is easily seen that the equilibrium mentioned before is not a simple one with only four compounds involved. Rather it involves many compounds and equilibrium is never actually reached, because in order to produce a desirable sulfonated oil the reactions must be ended when the maximum quantity of the sulfuric acid ester of the fat has been formed. The time required to reach this optimum varies with the temperature, the concentration of the sulfonating agent, and the ratio of sulfonating agent to fat.

Although we have just noted that the formation of a maximum amount of sulfuric acid ester is desirable, please do not infer that the side reactions are always suppressed as much as possible. The quantity of sulfuric acid ester present in a sulfonated oil largely determines the degree to which it disperses in aqueous emulsions. However, the presence of side reaction products often influences the useful application of an oil as well as its general characteristics. For this reason conditions are often deliberately set to favor to some extent one or more of the possible side reactions. This accounts for the wide variety of sulfonated products made from any particular fat or oil.

Because of all this, it is necessary to use an excess of sulfonating agent over that required to form the amount of ester which is obtained. This necessitates some sort of washing or neutralization to remove the excess acid which by its presence would not only render the final product unstable but might also damage the textiles to which the sulfonated oil was subsequently applied. This washing process may be carried out with water, sodium sulfate or sodium chloride solutions. Here again conditions of time, temperature and concentrations must be carefully controlled in order to obtain as dry a product as possible without excessively splitting the glycerides, hydrolyzing the desirable ester, or forming lactones or complex esters. Neutralization without washing is, as a rule, carried out only with sulfonated tallow, where the presence of large amounts of inorganic sulfates is often considered beneficial rather than deleterious.

Sulfonated oils as they come from the washing process are rather unstable. The acid ester has fat splitting properties and tends to increase the free fatty acid content, while the small amount of mineral acids together with inorganic sulfates and in some cases chlorides, and water, tend to hydrolyze the sulfuric acid ester and form saturated hydroxy acids. Consequently, such bases as sodium, potassium or ammonium hydroxide must be added in sufficient quantity to neutralize all the residual mineral acid, all the acid ester and at least some of the free fatty acid to guard against any possible hydrolysis on storage. The degree to which the free fatty acid is neutralized is governed by the use for which the finished product is intended. In some cases enough base is added (with heating) to neutralize all the fatty acid and to completely saponify the glycerides. Monopole soap is a product of this type. Monopole soap, which is sold under many different trade names, as you probably know, is a sulfonated castor oil completely saponified, used chiefly as a wetting out and penetrating agent in dyeing, particularly where direct colors are used.

While we are on the subject, let us consider briefly the sulfonation of castor oil. The predominant fatty acid of this oil is ricinoleic acid—



As you see there are two possibilities for sulfonation, the (OH) group on the eighth carbon atom and the ethylene linkage between the fourth and fifth carbon atoms. All sulfonated castor oils undoubtedly contain both types of esters. However, the properties of the oils vary considerably depending upon which type predominates. The resistance of a sulfonated castor oil to the effects of acid in a dyebath is particularly affected by the point at which the ester occurs. It is important, therefore, to control the type of ester formed and it has been found that by carefully controlling temperatures during sulfonation, the sulfuric acid can be made to react either at the hydroxyl or at the double bond.

Research has been carried on continually toward improvements in sulfonated oils, especially to increase their resistance to the formation of insoluble calcium or magnesium soaps in hard water. It was found rather early that as the combined SO_3 content increased, all other factors being equal, the tendency toward the formation of insoluble soaps decreased. Consequently, many methods were devised to obtain a higher degree of sulfonation. Among these methods were the use of inert diluents, which were removed from the finished product, the addition of some of the lower aliphatic acids, anhydrides, or halides during sulfonation, and the use of mutual solvents for the sulfonating agent and oil, such as liquid sulfur dioxide (SO_2) in which is dissolved sulfur trioxide (SO_3). By these methods and many others, oils containing high percentages of the sulfuric acid ester were obtained and some of them did exhibit much greater stability in hard water.

Another factor, however, also has been shown to affect the formation of insoluble calcium and magnesium soaps.

This is the total alkali content of a sulfonated oil, or the alkali combined as soap. When the total alkali is high, the formation of insoluble soaps in hard water is very rapid, but when the total alkali is low, the rate of formation of these soaps is greatly decreased. This has been explained by certain investigators by claiming that the hydrolysis of the soap in water facilitates a double decomposition reaction between the soap and soluble calcium or magnesium salts. On the other hand, the ionization of fatty acid is very small, thus retarding its reaction with these salts to form insoluble soaps.

It has also been found possible to so control conditions of sulfonation that oils are produced having a very small free fatty acid content and also a very small percentage of alkali combined as soap. This type of product is also fairly resistant to the action of hard water.

Many other methods have been used to eliminate the difficulties experienced with sulfonated oils in hard water. As the formation of calcium and magnesium soaps seems to depend on the presence of the carboxyl group of the fatty acids or upon the alkali soaps formed at this group, many attempts were made to block the carboxyl group.

This blocking is accomplished by substituting various groups for the (OH) of the carboxyl. For example, various esters may be formed or amides. Igepon T may be cited as belonging to this class of products. Here one of the (H) atoms of the amide is replaced by an alkyl group. A true sulfonic group is also introduced in the alkyl group by means of ethionic acid

$$\begin{pmatrix} H_2C{-}OSO_2OH \\ | \\ H_2C{-}SO_2OH \end{pmatrix}$$

Furthermore, various catalysts have been used in an attempt to obtain true sulfonation, direct sulfur to carbon linkage of the SO_2OH group. I have here an interesting product of this type. This is an sulfonated oleic acid, the combined SO_3 of which cannot be determined by the Hart Method. Even boiling for four hours under a reflux condenser with 4 normal sulfuric acid instead of the required amount of 1 normal acid will not break down this oil. The Carius Method, however, shows a high SO_3 content. A five percent emulsion in water of 310 grains hardness is very stable. Products of similar stability can be made from other oils.

The natural fats and oils are now being supplemented by products with fat-like properties not found in nature. Among these are the fatty alcohols produced by the reduction of fatty acids with hydrogen in the presence of suitable catalysts. Dr. Lehner will speak to you regarding the Gardinols and Brilliant Avirols made from these alcohols. Even more recently interesting sulfonation products made from mono esters of fatty acids and dihydroxy alcohols have been developed. If the fatty acid in these esters is unsaturated, they may be sulfonated either at the double bond or at the hydroxyl group or at both. If two moles of these esters are combined with the elimination of one mole of water, fat-like ethers are formed which may also be sulfonated. The products thus formed are resistant to hard water and show other properties which make them interesting for textile purposes.

All these new products are more or less synthetic and consequently somewhat more costly to manufacture than the sulfonated oils. In general, these new products have certain definite qualities which make them suitable for specific uses. However, none of these qualities are such that sulfonated oils cannot be made to exhibit the same qualities although not in all cases to the same degree.

During all the research that has been carried on, few, if any, new chemical reactions have been developed. Rather, various well known reactions have been utilized with perhaps some refinement of equipment to produce emulsifiable oils, fats, or fat-like materials for the textile industry. A survey of the patents and literature on the subject serves to confirm this.

Before concluding I should like to call your attention to the fact that it is possible to produce oils containing percentages of organically combined SO_3 too high for some textile applications. In finishing for example, the percentage of organically combined SO_3 should be just high enough to produce emulsions of the oil which are stable and compatible with the gums, starches and dextrines which are used. The desired body and softness produced in the finished fabric is due not to the sulfonated portion of the oil but to the neutral oil itself. The function of the neutralized sulfuric acid ester is to disperse the neutral oil in a fine stable aqueous emulsion and to so lower the interfacial surface tension between the emulsion and the textile fibers as to permit a quick and uniform distribution of the neutral oil throughout the fabric. The neutral oil itself has the requisite lubricating and softening properties. If, however, a finishing oil is so highly sulfonated that little or no neutral fat is present, then the finish imparted to the fabric lacks softness and is dry and papery.

Another case where too high an SO_3 content is not desirable is in oils for the soaking of silk for throwing. In this operation it is desirable to use only sufficient oil to soften the gum and to give such take-up, with complete exhaustion of the bath, that the thrown boil-off of the silk will be within certain specified limits. To accomplish this effect, it is generally conceded that an oil should be used having an SO_3 content just high enough to form a stable emulsion until the silk is entered into the bath when the emulsion should break just rapidly enough to insure even take-up by the silk, accompanied by softening of the gum and complete exhaustion of the bath in a reasonable soaking time. If, on the other hand, an oil is used having too high an SO_3 content, the soaking emulsion is so finely dispersed, that comparatively little take-up of the oil by the silk occurs. To obtain the proper softening of the gum

and the required thrown boil-off, it is necessary to use relatively large quantities of oil. This is decidedly uneconomical as most of the oil remains in the bath and is thus entirely wasted.

I have endeavored to bring to your attention, this afternoon, some of the current opinions regarding sulfonated oils, as well as to indicate the trend in the development of new products. Lack of time has forced me to present this subject in a rather brief manner. However, I hope that I have impressed you with the complex nature of these sulfonated oil products and with the idea that choosing the type of sulfonated oil best suited for any particular process is not a simple matter. More detailed discussions with the manufacturers of these products regarding the factors influencing their general properties and application will, I am sure, help you in the solution of many of your problems.

Discussion

Chairman Cady: Is there any discussion of this paper?

Mr. Harry W. Ericson: In discussing the placing of the sulfonic groups on either the ethyl links or hydroxyl, you demonstrated that one made a rather cloudy emulsion and one of them a very clear emulsion. In which one of those is the sulfonic acid present?

Mr. Davis: It isn't a sulfonic acid—the ester formed at the hydroxyl group gives the clear one, and the double bond gives the cloudy one.

Dr. Jos. F. X. Harold: I should like to ask the speaker if there has been any study made of the size of the dispersed dye particle and the degree of absorption by a fabric.

Mr. Davis: The size of the dispersed dye particle?

Dr. Harold: No, the dispersed oil particle.

Mr. Davis: There has been some but I haven't the authorities to quote from here.

Dr. Carl Z. Draves: If an aqueous solution of the usual monopole oil and a solution of the basic dye are poured together, the two substances mutually precipitated each other. Will this emulsion here which remains clear in acetic acid precipitate a basic dye?

Mr. Davis: It is apt to, because the pH of the emulsion is considerably under 7. In other words, the emulsion is fairly acid.

Dr. Draves: Yes, but you have an excess of acetic acid, haven't you?

Mr. Davis: Oh, yes, I have acetic here, but I mean without acetic acid in water alone—I see what you mean. No, that shouldn't be.

Dr. Draves: Have you tried it?

Mr. Davis: I haven't with basic dye because this has been applied mostly with direct colors.

Dr. Samuel Lenher: I think I can answer Dr. Draves' question.

I don't think the basic dye would be actually precipitated with an excess of acetic acid; only a theoretical amount is necessary to combine with the basic dye ion. The excess of sulfonated oil would act as a dispersing agent for the insoluble compound formed with the basic dyestuff and you will get a clear dispersion after the precipitate is first formed.

Dr. Draves: My question, though, is if they are present in nearly equivalent amounts. I know if you use a very large excess of sulfonated oil, you can redisperse that precipitate with an excess of oil. My question is if they are present in nearly equivalent amounts will they obtain a clear solution?

Mr. Davis: I think you get precipitation there, don't you, Dr. Lenher?

Dr. Lenher: Yes, you do, Mr. Davis.

Chairman Cady: Is there further discussion?

The next speaker will be Dr. Samuel Lenher, of the du Pont Company, who will speak on, "Development in the Application of Fat Alcohol Sulfates." Dr. Lenher!

. . . Dr. Lenher presented his prepared paper . . . (Applause).

Dr. Lenher's paper will appear in an early issue of the Reporter.

UNEMPLOYMENT REGISTER

(Continued from page 629)

A-B-C-1

Education—Graduate Industrial Chemical Engineer, Pratt Institute—1911.

Experience—One year as plant control chemist, 4 years as laboratory chemist with gas company, 13 years as plant chemist with bleaching, dyeing and finishing plant. (Rayon and cotton piece goods). Formulated processes and put them into plant operation, 1 year as chemist and demonstrator for dyestuff company, 1 year as superintendent colorist with print works printing linen and rayon, 1 year as director of testing laboratory for national dry goods concern.

A-B-E-1

Education—B.S. in chemistry at C.C.N.Y. Working now on M.A. at Columbia.

Experience—7 years as dye tester and color matcher for dye manufacturer; 6 months skein silk and rayon dyer; 4 years textile chemist and dyer for cotton finishing concern; 2 months boss bleacher and 4 years as teacher of organic chemistry and dyeing. Age 38, single.

(Continued on page 640)

Proceedings of the American Association of Textile Chemists and Colorists

New Possibilities in the Lubrication of Textile Fibers*

By CHARLES B. ORDWAY, M.S.*

**Assoc. Prof. of Tex. Chem. & Dye., Alabama Polytechnic Institute*

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WE SPEAK of lubricating or "oiling" of various textile fibers and yarns, but we are actually "relubricating" the fibers or yarns if there has been any dyeing, kier boiling, or bleaching operation carried out previously. To "relubricate" any fiber, man has used the most available material and has scarcely considered the make-up of the original lubricant and waxes that nature put on these textile fibers.

These original lubricants and waxes in their natural state if purified and placed on a clean fiber would not be entirely satisfactory for all manufacturing purposes but they are naturally fitted to the physical and chemical make-up and requirements of each particular textile fiber and possess many advantageous properties for these reasons.

Research has shown us the many wonderful inner workings of fibers and it appears that they could be lubricated advantageously by using products as nearly the same as the original lubricant if it can be made whereby it will work satisfactorily throughout all the manufacturing processes involved.

In cooperation with the Glyco Products Co., Inc., research has been carried on through their Fellowship at the Textile Chemistry and Dyeing Laboratories of the Textile School of the Alabama Polytechnic Institute, for the development of synthetic lubricants for textile fibers. The preliminary study may be put in a condensed form as a large majority of those present are familiar with most of these points and details will be omitted for this reason.

Properties of the natural lubricants and waxes in cotton fibers:

Desirable Properties

1. Waxiness, high resiliency, and strong "pulling quality" of any good character of raw cotton from the upland short staple (7/8") to the long staple, Delta and American Egyptian types.

2. High hygroscopic or moisture pick-up of the best grades of raw cotton.

3. Natural lubricants and waxes act as a protection as well as a lubricant both internally as well as externally for cotton fibers.

Undesirable Properties

1. Insolubility in cold or hot water and the necessity for their removal by the assistance of strong alkalies, etc., in case the cotton is to be dyed or bleached. Any natural wax or lubricant that may remain on fibers causes the retarding of most all of the types of dyestuffs except the basics and this may result in unevenness, streaked dyeing and poor money value received on dyed shade.

The dye or bleach liquor does not penetrate the fibers without being thoroughly scoured or is caused to penetrate by means of some "wetting out" agent. This is because of the insolubility of these natural products on fibers.

Present Day Lubricants

The selection of these lubricants in modern usage has been mainly an accumulation over a period of time.

They may be divided up into two chief classes:

1. Mineral oil lubricants.
2. Soluble and sulfonated vegetable oils (animal oils may be included in this group).

Mineral Oil Emulsions: These are usually a blended mix of the mineral oil and some type of vegetable or animal oil. This type endeavors to combine the most valuable properties of the two main classes just mentioned and some of the manufacturers have reached a high level of accomplishment on this.

Undesirable Properties

1. The aged or highly oxidized vegetable oil and any lubricants containing mineral oils are rather difficult to remove from the cotton fibers and necessitate a harsher scouring medium as well as the use of solvents.

2. Most of these types of lubricants are odor forming

*Presented at Saturday afternoon session, Annual Convention, Chicago, Sept. 9.

and the present-day market is now offering deodorants for this trouble mentioned.

3. The oxidation or ageing of these products may result in a resinous or gummy feeling on the fiber and this proves troublesome in manufacturing.

4. The mineral oils possess poor electrical conductance and low hygroscopic properties and may prove dangerous in case of fire starting in the carding and spinning operation.

5. The vegetable oils possess fairly good electrical conductance, fair hygroscopic properties but have a tendency to become sticky or gummy on ageing due to their oxidation and this generally acts as a deterrent to smooth carding and spinning operations.

Desirable Properties

1. These types of oils possess highly desirable lubrication properties for the fibers and assist in decreasing the brittleness of the fibers as they are being carded and combed out straight, preparatory to the spinning operation. The mineral lubricants act more externally on the fibers while the vegetable types tend to penetrate and lubricate both internally and externally on the fibers though the lubrication is not as smooth and soft as that of the mineral oils from an operation viewpoint.

Ideal Fiber Lubricant

An ideal synthetic lubricant should possess the best features of the natural lubricants such as:—

(1) waxiness without gumminess; (2) high hygroscopic properties; (3) good resiliency of raw cotton stock. In addition it should possess (4) high electrical conductivity to lessen danger of fire and lower the amount of "fly" during the carding and spinning operations. Other properties that are desirable are as follows:

5. Fire retarding.

6. Smooth internal and external lubrication to promote a smooth, soft, and flexible fiber which should lower the fiber breakage in manufacturing.

7. Non-gumminess when dried on fiber.

8. Non-corrosiveness.

9. Inexpensiveness in application as well as cost of material used.

10. Simplification of the method of application so as to meet the varying conditions met in mill practice.

11. A lubricant should be water soluble and easy to remove by a hot water bath only.

Taking all these factors into consideration, the glycol bori-borates were investigated and experimental work duplicated plant procedure as closely as possible as to formulae, handling and working conditions used.

Experimental tests were first carried out on the three types of dyes (directs, sulfurs, and vats) used in dyeing cotton raw stock by dyeing in the pots on water baths and then carrying formulae so secured onto a small size laboratory raw stock dyeing machine so that the findings could be checked. Methods used were as follows:

Raw cotton was boiled out previous to dyeing by two methods: (1) soda ash (sodium carbonate) and (2) sulfonated castor oil. Then sets of dyeings were made on cotton from these two types of "boil-outs" as there is considerable difference as to the amount of natural waxes and lubricants removed in each case. The regular dyeing formulae were used as recommended by the makers of dyestuffs, then a thorough washing to remove all traces of chemicals used and in the final wash water the following compounds were added for each set of tests:

5% common salt (NaCl), 10% common salt on all types of dyed raw cotton.

2% sulfonated castor oil (75% commercial) on all types of dyed raw cotton.

1½% Aquaresin GM (glycol bori-borate) on vats and sulfurs.

1% Aquaresin GM (glycol bori-borate) on directs.

These percentages were arrived at after a series of experimental tests as to the amounts that give the closest basis of comparative results.

On completion of these various experimental tests in the A.P.I. textile laboratories, the work was then transferred to a mill scale and the raw cotton used there was of an excellent character, ⅞" to 1" fiber stock. The regular mill processing was carried out as follows: (1) boil out with sulfonated castor oil; (2) dyeing operation, dropping dye-liquor and washing with cold water for required time to free the dyed cotton of any chemical used; (3) then warming up a final clear water bath to 120° F. and adding 5% salt and running for 15-20 minutes, draining, hydro-extracting, drying, baling and sending over to the opening and carding department at the end of a few days. This plant used a mineral oil system and the oil was sprayed into the opener box onto the dyed stock for additional lubrication purposes.

Experimental runs were made first on heavy sulfur shades since the raw cotton fibers are given the harshest treatment and suffer the largest loss of natural lubricants in this dyeing method due to the high temperatures of dyeing operation and the soda ash and sodium sulfide dyebath. Due to this harshened condition of the raw cotton stock, 1½% of Aquaresin GM was used in place of the 5% salt wash as stated in the regular mill process for the final wash at 120° F., the cotton was hydro-extracted, dried and baled. The use of the mineral oil spray was omitted as used on regular mill runs and the carding and spinning results were reported as satisfactory and the stoppage of manufacturing processes was kept at a minimum as required of the regular mill runs.

Runs of the sulfur black and direct colors were equally satisfactory. For the directs there was only 1% Aquaresin GM used in place of the 5% salt wash and mineral oil spray.

Results secured from the regular mill size experimental operation were highly gratifying and were superior to

some of the experimental data secured on the small size laboratory raw stock machines. Tabulation of the results from all the experimental work run on various types of raw cotton stock indicate that Aquaresin GM possesses many of the desirable properties of an ideal lubricant for fibers.

First, it tends to restore the dyed cotton fibers to their original waxy and resilient condition. Second, it possesses approximately the same hygroscopic properties that the original good character raw cotton has; and third, it is non-corrosive to the metallic card clothing while the common salt washes that are usually run in connection with the mineral oil spray are rather corrosive and increases the replacement costs noticeably in some plants. Fourth, this product has a high electrical conductivity. Fifth, if sprayed on, it would be best to use about a 25% solution (water soluble) and it should assist in decreasing the "fly" and has fire retardency properties.

The moisture pick-up or regain shown on all dyed samples processed with Aquaresin GM was about equal to that of the original raw cotton when a good character of cotton was used and higher than the original raw cotton on the "air-dried" or "perished" types, and mid-way between that of the samples processed with 5% and 10% salt wash and final mineral oil spray.

Aquaresin GM is water soluble and can be removed by hot water bath at 170-180° F. or with a few ounces of soap or milder alkalies at lower temperatures. This property indicates that it should possess real value for rayon lubrication as well as cotton, and this work will be carried out at a later date.

Users of good character raw cotton are naturally interested in maintaining the operation conditions at a high level of efficiency and wish to keep their finished yarns with a good, well lubricated feel and fibers that are resilient, soft and flexible. These results are maintained to a high degree by this proposed method of processing. But to those users of off-grade raw cotton that might be classed as "air-dried," "perished," "export-compressed," "weathered," etc., types, they have poor running cotton to start with and their troubles in the carding and spinning may be improved greatly by the use of a type of synthetic lubricant like Aquaresin GM that will restore "perished" fibers to the highly desired waxy, high hygroscopic powers, resilient, flexible and well lubricated condition necessary to smooth running conditions in the plant and keeping the breakage in carding and spinning to a minimum.

Discussion

Chairman Cady: Is there any discussion of this paper?

Mr. Schroeder: Are these products in regular production?

Professor Ordway: They have them on initial production.

Chairman Cady: Is there any further discussion of this paper? (There was none.)

UNEMPLOYMENT REGISTER

(Continued from page 637)

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—Educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following; celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

B-7

Experience—4 years as assistant to manager in ribbon mill; 2 years as boss dyer on veils, chiffons and silk skeins; 5 years as boss dyer on ribbons and skeins (cotton and silk); 7 years as boss dyer on spun silk (pure dye and fast) resisted colors; last 12 years as hosiery dyer on silk and cotton, silk-cotton, rayon or wool. 50 years old, married. References.

B-8

Education—Chemistry and Dyeing Department, Philadelphia Textile School.

Experience—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

B-9

Experience—Hosiery dyer with fifteen years' experience on high grade silk hosiery; familiar with all types of machines. Age 43, married. Will go anywhere. References furnished.

AMERICAN
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REPORTER

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PRODUCTIVE MACHINERY

UNDER the new regulations approved for the cotton textile industry, it becomes necessary for a manufacturer, in order to increase his productive machinery to obtain a certificate from the NRA administrator certifying that such installation will be consistent with the aims and purposes of the recovery act. Without this certificate it will be impossible for the cotton textile producers to install new machinery except to replace old machinery (unit for unit). These regulations as approved provide that:

1. Persons engaged in the cotton textile industry register their productive machinery;

2. Prior to the installation of additional productive machinery by persons engaged or engaging in the cotton textile industry, except for the replacement of a similar number of units of productive equipment, or to bring the operation of existing productive machinery into balance, such persons shall secure certificates from the Administrator certifying that such installation will be consistent with effectuating the policy of the national recovery act during the period of the emergency, and

3. A certain procedure shall be followed in applying for such certificates and the making of recommendations by the cotton textile industry committee as to the granting or withholding of such certificates by the Administrator.

It is believed that these provisions as announced by General Johnson are the beginning of a new policy of forbidding the financing of new plants or the expansion of old ones as long as the consumption is below the capacity of existing machinery. To our mind, this is a sound principle for long term application and although it will work hardship on some at the present time, particularly machinery manufacturers, we believe that in the long run it will have a healthy influence on stabilizing our economic structure.

WAR ON "CHISELERS"

THE first of last week President Roosevelt and NRA Administrator Johnson took advantage of the powers granted them by Congress by providing fines of $500 and imprisonment of not more than six months or both for violators of NRA agreements. The reason for this action was that there are an increasing number of complaints being registered and it is hoped that this drastic step will put a stop to them. Most of the complaints so far registered have been against the smaller merchant. This step by the President and the regulations issued by General Johnson are considered by many to be the most significant step so far taken in the current rehabilitation program.

The Executive order called attention to the fact that no one can "falsely" display the emblem of the NRA or under conditions contrary to the principles of the industrial recovery program. One of the provisions included in the regulations stipulated that in the event the Blue Eagle was recalled from any merchant he would not be deprived of the right to sell articles marked by manufacturers with the Blue Eagle insignia. To date there have been only three Blue Eagles recalled, two from New York State and one from the middle West, but there have been hundreds of complaints made.

Evidently the 100 per cent support of industry which had been hoped for has not been forthcoming and to bring the delinquents into line it has been necessary to invoke the drastic punishments mentioned above. It is to be regretted that the Administration cannot have the wholehearted support of all industry, employer and employe, to determine absolutely the value of the recovery act. Its success will be hindered considerably by the actions of the "chiseler."

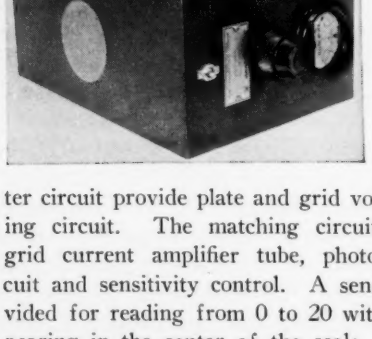
It would be extremely naive to believe that, having guided America's destinies for many long years, Greed and Stand Pat-ism would be satisfied to step aside now and let the nation enjoy its new leadership. They spread their seditious gospel. They use every means at their disposal to prevent the re-born nation from reaching its destination. Calling in loans, refusing to extend long-term credit to merchants and manufacturers, transferring their hoarded money abroad, engaging the services of high paid lawyers in the fight against the NRA codes, mobilizing the cohorts of disgruntled politicians overthrown by the great national uprisal of last November. . . . It would be impossible, indeed, to describe all the tricks resorted to by Greed and Stand Pat-ism. Nothing is too low, nothing too treacherous, nothing too cruel in the estimation of the men who lead their forces.—*Cornelius Vanderbilt in recent radio address.*

Photo-Electric Color Matcher

The Westinghouse photo-electric color matcher is a portable, comparatively inexpensive device for matching colors. It is arranged to compare samples at three points of the visible spectrum indicating whether two samples are matched. It does not analyze samples into the respective constituents. The color matcher is especially valuable for the following applications: Sample painted and lacquered paddles can be tested with great accuracy or a standard paddle can be compared with finished wall of a house with equal accuracy. Differences in porcelain and enamel tiles hardly discernible to the eye can be segregated by the color matcher with little difficulty. It is especially good for comparing white tile, the most difficult of all color tile problems. Its value in the field of printing and lithography is indispensable for paper stocks and inks. It can also be used for matching dyes, pastes, food, coffee, etc.

The construction of the color matcher permits its use in any position. In general, it is intended to be placed on the samples to be compared or its position reversed so that samples may be placed on the aperture for comparison. Light weight and a long flexible extension cord permit adjustments in its position as required.

Either light or dark samples may be tested, the sensitivity of the unit allowing the matching of even very black surfaces. On the other hand, the range of operation is such that very brilliantly colored surfaces are within the range of the instrument. Condition of surface, dull or bright, does not affect the color matcher.



The power supply is operated entirely from a 110-115 volt, 60 cycle source, no batteries whatever are required though they may be substituted if desired. A rectifier tube and filter circuit provide plate and grid voltages for the matching circuit. The matching circuit consists of a low grid current amplifier tube, photo-tube, coupling circuit and sensitivity control. A sensitivity meter is provided for reading from 0 to 20 with the number 10 appearing in the center of the scale. There are two sets of numbers on the meter so that it may be read in the usual way or inverted.

The optical system is independent of daylight or external artificial light. It is made up of four major parts, the lamp, a set of color filters, a lens and mirror, and an integrating chamber. The photo-tube is the common unit between the optical and electrical systems. The lamp is the standard concentrated filament type and is run at low voltage to insure long life. The three-color light filter permits comparison at separate color points, namely, blue, green and red. These three represent the short, medium and long wave lengths in the visual spectrum. The lens and mirror bring the light rays to the sample, and the white, integrating chamber brings the rays to the photo-tube, which has a color characteristic to give excellent operation with the lamp source.

A three position color screen permits comparison to be made between a sample and a standard in each of three bands of the spectrum, blue, green and red. In comparing a sample with a standard, each band of the color screen is used. Comparison consists of identifying the sample as "lighter," "darker," or "matching" the standard in each band.

Carbanthrene Printing Powders

A new era of economy is said to be opened to the color shop with the introduction of a complete line of vat printing powders by the National Aniline & Chemical Co., Inc.

These Carbanthrene printing powders differ distinctly from the orthodox types of vat pastes with which the printing trade has had to contend throughout past years. All of these new printing powders are instantly dispersable and can be stirred directly into the "printing gum" requiring no "pasting up" with water or other solvents. Because of their finely divided state and the action which follows while the powders disperse in the printing gum, an extremely homogeneous and non-specking paste is said to be obtained. As the powders remain unchanged indefinitely instead of drying out, settling, caking on container sides or freezing during the winter months, difficulties due to these common characteristics of pastes are eliminated.

Accurate weighings of these vat printing powders assure a closer check on actual color shop consumption and a more positive adherence to established standards as successive patterns are returned for "repeats." It is claimed that penetration is achieved to a degree not as yet attained by other forms of vat colors. Fine lines and scroll work possess the same depth and density of color as do broad stripes and open work.

Brighter colors, sharper and clearer prints with the assurance of penetration coupled with the elimination of waste resulting from the archaic dipping method, are said to establish a new era of efficiency long sought for in the color shop.

General Releases

The General Dyestuff Corporation has issued cards on the following products:

I. G. 769—shows all fast-to-light direct colors which are comprised in their Fastusol "L" and Fastusol range, the first one containing the 32 fastest types, whereas the Fastusol range contains 28 more brands which range slightly lower in fastness to light. The shade card illustrates these 60 dyestuffs in three different strengths and also gives a number of combination shades.

I. G. 757—Palatine Fast Yellow 5 G. N, an addition to the series of Palatine Fast colors, which is said to

produce a bright greenish yellow of very good fastness to light, water, saltwater and washing; it is further claimed to have remarkable fastness even to fulling. It is said to dye very level and is useful as a shading color for combination shades. It is recommended by the manufacturer for the dyeing of piece goods for men's wear and ladies' goods, of carpet and knitting yarns, and also for the dyeing of loose wool and slubbing which has to stand a medium fulling.

Copies of the above cards may be obtained on request to the General Dyestuff Corporation.

New Ciba Circulars

The Society of Chemical Industry in Basle has lately issued the following:

Circular No. 399. *Ciba Bordeaux 2RN pat.* This type is somewhat yellower in tone than the older type Ciba Bordeaux 2R and is claimed to have very much better fastness to light. It is also said to have very good fastness to washing, fulling, chlorine and perspiration. This new product is well adapted for goods that are to be bleached, but it is necessary to take the proper precautions for the kier boiling. Ciba Bordeaux 2RN is recommended for cotton goods in all stages of manufacture, also for rayon as well as true silk. In the case of silk, however, the dye is not entirely fast to boil-off. Cotton and rayon fabrics are printed by the usual procedure. Dyed fabrics may be discharged by means of Hydrosulfite RA Ciba and Discharge Salt Ciba W to a clear white. In printing pure silk it is recommended to pass the goods through an oxidizing bath after steaming.

Circular No. 402. *Cibacete Blue BRF powder.* This new dyestuff dyes acetate rayons a much purer and brilliant blue than the old type Cibacete Blue BR powder. The fastness to light is said to be better than the older types; exhaust and levelling remain the same. This type is especially recommended by the distributors as the blue element in combinations. The fastness to washing, water and cross dyeing are said to meet all practical requirements. In artificial light the shade becomes just a trace duller and weaker. It is dyed in the usual way in a bath containing soap or soluble oil. Cotton and rayon are left undyed but silk and wool are tinted, but these may be cleared by the use of hydrosulfites. This new dyestuff is also well adapted for direct printing, but the dyed shades are not dischargeable.

Sample Card No. 1082. *Dischargeable Fashion Shades* with Neolans and acid dyestuffs on wool muslins. The discharge prints show, in order, combinations with Neolans, Neolan types, combinations of Neolans and acid dyes and acid dyestuff types. The shades are dyed by the usual method used for Neolans, but when Napthochrome or Cloth Fast colors are used, then the dyeing is done first with acetic acid and later the sulfuric acid is added. The discharges were made with Hydrosulfite RWS Ciba.

Sample Card No. 1093. *Ciba Blue GBH, BH, 2RH, 3RH.* This card illustrates the new type GBH in comparison with the older types. Ciba Blue GBH is distinguished from the former types by its decidedly greener shade. It is said to be well adapted, like the others, for the production of inexpensive medium and dark blues having good fastness to light and washing. All the dyestuffs shown find considerable use in the dyeing of overalls, linings, knit goods, sewing threads, silk and rayon, etc. Both the new type as well as the older types are dyed either by the regular hydrosulfite process or by the combined hydrosulfite-sodium sulfide process or by the sodium sulfide-glucose process.

Copies of these sample cards may be obtained from the Ciba Company, Inc.

Adopts 5-Day Week

In order to give full support to the NRA program, the National Oil Products Company, Harrison, New Jersey, makers of industrial sulfonated oils and other animal and vegetable oil products, has arranged its production schedules and working hours on the basis of a 5-day week. Its offices, laboratories, and plant will be closed on Saturdays beginning October 1st.

STATEMENT OF THE OWNERSHIP, MANAGEMENT, CIRCULATION, ETC., REQUIRED BY THE ACT OF MARCH 3, 1933, OF AMERICAN DYESTUFF REPORTER published bi-weekly at New York, N. Y., for October, 1, 1933.

State of New York, County of New York, s.s.:

Before me, a Notary Public in and for the State and county aforesaid, personally appeared Alfred P. Howes, who, having been duly sworn according to law, deposes and says that he is the Publisher of the AMERICAN DYESTUFF REPORTER, and that the following is, to the best of his knowledge and belief, a true statement of the ownership, management (and if a daily paper, the circulation), etc., of the aforesaid publication for the date shown in the above caption, required by the Act of March 3, 1933, embodied in section 537, Postal Laws and Regulations, printed on the reverse of this form, to wit:

1. That the names and addresses of the publisher, editor, managing editor, and business managers are:

Name of—— Post office address——

Publisher—Alfred P. Howes, 440 4th Ave., New York, N. Y.

Editor—Prof. Louis A. Olney, Lowell, Mass.

Managing Editor—Norman A. Johnson, 440 Fourth Ave., New York, N. Y.

Business Manager—None.

2. That the owner is: (If owned by a corporation, its name and address must be stated and also immediately thereunder the names and addresses of stockholders owning or holding one per cent or more of total amount of stock. If not owned by a corporation, the names and addresses of the individual owners must be given. If owned by a firm, company, or other unincorporated concern, its name and address, as well as those of each individual member, must be given.)

Owner: Howes Publishing Company, Inc., 440 Fourth Ave., New York, N. Y.

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3. That the known bondholders, mortgagees, and other security holders owning or holding 1 per cent or more of total amount of bonds, mortgages, or other securities are: (If there are none, so state.)

None.

4. That the two paragraphs next above, giving the names of the owners, stockholders, and security holders, if any, contain not only the list of stockholders and security holders as they appear upon the books of the company but also, in cases where the stockholder or security holder appears upon the books of the company as trustee or in any other fiduciary relation, the name of the person or corporation for whom such trustee is acting, is given; also that the said two paragraphs contain statements embracing affiant's full knowledge and belief as to the circumstances and conditions under which stockholders and security holders who do not appear upon the books of the company as trustees, hold stock and securities in a capacity other than that of a bona fide owner; and this affiant has no reason to believe that any other person, association, or corporation has any interest direct or indirect in the said stock, bonds, or other securities than as so stated by him.

5. That the average number of copies of each issue of this publication sold or distributed, through the mails or otherwise, to paid subscribers during the months preceding the date shown above is.....(This information is required from daily publications only.)

ALFRED P. HOWES, Publisher

Sworn to and subscribed before me this 28th day of September, 1933.

(SEAL) CAROLINE ESSENBREIS

(My commission expires March 30th, 1935.)

A Rapid Method of Determining the Nature of

"Mixability" of Raw Silk

By **CHESTER W. MEYERS, B.T.C.**
Associate Dyer and Supervisor of Raw Silk Testing
Massachusetts Knitting Mills, Boston, Mass.

ONE of the greatest difficulties experienced in the dyeing of full fashioned hosiery arises from the mixing of different lots of silk in the knitting. This mixing usually results in a pronounced variation in shade in the portions of the stocking that are knit from the separate lots. Thus one part of the stocking will be lighter or darker than the other, and where this difference is great it results in a larger proportion of seconds. Once the lots are mixed, there is nothing the dyer can do to make both portions look alike, so naturally the only solution is to keep separate in the knitting department the lots which are going to cause a variation in shade.

These variations may be due to any number of conditions such as old and new silk; silk soaked with different amounts of soaking oil and with different oils; differences in twist, etc. These cases are elemental and in an efficiently conducted organization can be easily eliminated.

This article, however, is devoted to the cases that arise from the variations in shade due to the nature of the silk, and provides a short, simple test for keeping separate the silks which cause great variation in shade and for mixing silks which cause little or no variation.

One question which arises in the mill is, "If I make the legs from the last lost, and I foot them with the new lot, will the two portions match? Will they dye the same shade?" To actually knit a stocking or a set, and boil-off and dye to see if this is true, is too long a process. Also for the small mill to purchase, and conduct experiments, with the expensive "nature machines" on the market, is not appealing. What the mill man wants is a quick inexpensive method of testing nature or "mixability."

Regardless of what causes this difference in shade, which we attribute to "nature," it arises in the dye bath. Some silks seem to have a greater affinity for dye than others. Thus, as the nature of a silk varies so will the amount of dyestuff absorbed by the silk vary. Since this is true, what could be more logical than dyeing small sample skeins of the silk before knitting, and comparing the amount of dye taken up by the skeins of different lots to see whether they can be mixed or not. We will concede that matching small skeins of silk to ascertain the amount of dye taken up by each would be a task that even a dyer would shun, and is practically impossible. Still, if more dye is taken up by one skein than is taken up by another, it should be noticeable somewhere; and it is noticeable in the solution left after the dyeing.

Thus if we compare standard samples in Nessler tubes against the solution left after dyeing, we can get an accurate estimate of the amount of dye taken up by each skein and can compare this against the amount taken up by any lot of silk we are running or intend to run. The dyeing does not necessarily have to be hot. The skein may be immersed in a cold dye solution for a definite length of time and then removed and squeezed to remove excess dye solution. Dilute dye solutions must be used to get the best results.

One method tried in the raw silk testing laboratory at the Massachusetts Knitting Mills and found to be applicable was:

Select a dyestuff, preferably an acid color, used by the dyer in the mill, and make up a stock solution of about .01%. From this stock solution a series of color standards are prepared showing varying percentages of the dyestuff.

No.	*cc. of Stock*	*% Dyestuff*	100—*% of Dyestuff* *A.V.*
1	25	100	0
2	22½	90	10
3	20	80	20
4	17½	70	30
5	15	60	40
6	12½	50	50
7	10	40	60
8	7½	30	70
9	5	20	80
10	2½	10	90

The numbers in the left hand column refer to the ten standards containing the various quantities of stock solution as set down in the second column. We arbitrarily

call Number 1 tube, 100%, Number 2, 90% and so on down to Number 10 or 10%. Column 4 refers to the absorption value (A.V.) of the silk. If the skein takes up no dye from the solution the remaining solution will compare with Standard Number 1 and the silk will have an A.V. of zero. If dye is taken up by the skein and the solution compares with Standard Number 5 we have an absorption value of 40.

The standards are made up in 50 cc. Nessler tubes and diluted to the mark. These standards are very susceptible to fading so they should be protected from the light. If standards comparable to them can be made up of some inorganic salt that will give the same color as the dyestuff used, and which will not fade, it is more desirable. Solutions of copper sulfate sometimes give the same color as some blue dyes used as standards, and solutions of potassium dichromate can be used for some yellow colors. If a good dyestuff is used and the solution is sufficiently dilute, there should be no trouble in "reading" the colors. In the tests made at the Massachusetts Knitting Mills we have found that either blue or yellow dyes are the easiest to read. Reds, oranges and browns are more difficult.

Taking the samples is important: Each sample should weigh 14 denier but an allowance of 0.25 denier would not be too great. The samples are placed in small beakers and 50 cc. of the stock solution is added. The skeins are stirred around in the dye for a definite length of time then 25 cc. of the solution is removed in a pipette, transferred to a Nessler tube, diluted to 50 cc. and compared with the standards. A number of samples are taken and the results averaged. The average is taken as the absorption value (A.V.) for the lot.

Two lots which have the same A.V. may be mixed without having any variation in shade in the stocking. The difference in A.V. that is allowable before too serious a deviation in shade occurs, will have to be worked out for each individual mill.

The test is quite simple to make, the whole thing taking only about ½ hour. After a little practice one should become quite proficient at reading the colors. It does not require an expert color matcher or analyst to do this. Theoretically, the test is quite sound. The same conditions are used that are experienced in the dye-house. In fact, if the cold dyeing does not give accurate enough results in the mill at which the test is applied, the silk may be dyed at a boil providing the volume of water is kept kept constant; or the silk may even be degummed first in a separate bath and then dyed. If these methods are used the length of time for the test becomes about 1½ hours. If the tests are made cold the absorption values will of course be lower than if they are made at a boil. All tests should be run at the same temperature in order to have comparable values.

Other factors enter into consideration in this test that cannot be neglected and of course require additional machinery to be determined. The two main considerations are the average denier of the silk and the color of the raw silk. It would not be considered advisable to mix a dark cream or a dark ivory silk with a white and if the A.B. of two silks is the same, but the average denier varies too much, don't expect good results if these are mixed.

If this nature or "mixability" test is carried on in conjunction with the regular raw silk tests the results obtained will be appreciably more accurate. The nine meter evenness test recommended by Warren P. Seem gives a very good check on the average denier of various lots.

The author would be only too glad to answer any questions which arise in the mind of anyone interested in this test, would welcome criticism and would be interested in results obtained.

CULTIVATING OUR DYES TRADE

(Continued from page 628)

An importing house located in Mexico City, Mexico, will arrange to make purchases of American dyes and fillers, and will also take an agency. (Inquiry No. 4451)

American manufacturers registered on the Department of Commerce's "Exporters' Index" will be furnished all details pertaining to these trade openings upon request giving the numbers, addressed to the Bureau of Foreign and Domestic Commerce, Washington. In order to secure registration on the index referred to manufacturers are required to execute what is known as "Form No. 57," which may be had promptly upon application to the Department of Commerce. This blank is self-explanatory and when returned to the bureau serves to register the United States manufacturer on the department's "Exporters' Index," when it will be sent all reports and confidential information pertaining to its specific line of products received from the department's representatives abroad. There is no charge for this service.

The three prime essentials in serving the Latin-American trade are (1) cultivating the trade—which means selling the goods, (2) serving the markets, and (3) proper packing in order that injury and deterioriation in delivery be prevented.

The most important of these, of course, is the actual selling of the goods. And this phase of the business embraces in turn prices, terms, credits, methods and delivery. While we are the natural and logical supply source for these countries it must always be remembered that we are under the necessity of meeting and beating competition—especially German competition—Germany for many years having practically controlled these markets for dyes, dyes-making materials and related products, and it is today fighting fiercely to regain them, price-cutting being one of its effective weapons. So that American producers of the coal-tar products have a price-market to deal with in all of these countries—and this is really more important than quality to many of the countries, although it is claimed that our growing dyes trade with Argentina is built almost entirely on quality. In this respect that country differs radically from all of the other Latin-American nations.

Terms and credits naturally cut an important figure in our dealings. Here we touch upon a phase of trade with these countries that has served to keep down our export totals for many years. The Latin-American buyer, as a rule, resents and objects to paying cash against shipping documents and thirty days' credit has no attractions for him—in fact, many dealers and distributors consider it a reflection upon their standing, integrity and honesty to ask less than sixty to ninety days. As a matter of fact, Germany is well known to extend upward of six months' time on sales to responsible houses. This attitude on the part of Latin-American importers applies to all purchases from outside the respective countries. This means, above all things, that our exporters should have a care in selecting houses or dealers to handle their products. Fortunately, today through our branch banks, commercial agencies, the consular service and the Department of Commerce we may determine fairly accurately the standing and responsibility of dealers in Latin-America.

How may we best sell the goods?

Three methods are being used, all more or less successfully. Selling direct through mail contacts; selling through export commission houses (of which there are a number in each of our ports of shipment), and using travelling salesmen who, in most cases, carry sample colors and shade cards as "side lines" with other, *but non-related,* products.

The writer, by careful inquiries, has endeavored to ascertain the method which appears to appeal to the greatest number of our dyes products exporters, but has been only partially successful. It seems to be true, however, that the most important and most successful manufacturers and exporters—those exporters who ship the bulk of our dyes products—prefer covering these markets through the export commission houses. This is not surprising when we consider that these commission houses practically take over the trade and all details—secure the orders, pack and ship the goods, arrange terms of payment and credits, look after collections—in fact, handle practically every detail of the trade abroad on an agreed-upon commission basis, taking all responsibility in the transaction. Dyes manufacturers and exporters will realize at once the very considerable advantage in dealing with these trade representatives, saving the manufacturer all concern over the other end of the export deal. It is conceded by our best-informed export authorities that dealing through export commission houses has many advantages not possible through the use of any other plan.

Packing and shipping mean much in serving the Latin-American dyes importers. To an extent equalled only by the export of some food products our dyestuffs require the closest possible attention to packing requirements. All shipments to South and Central America pass through the equatorial zone of penetrating heat and dampness, and in order to prevent injury and serious damage must be packed in damp-proof containers. The importance of this cannot be overstated. In this connection it will be helpful to note that the Department of Commerce Transportation Division is prepared to confer with shippers on the proper packing and shipping of dyes materials, point out the essential requirements for ocean freight shipments of these products, and go into the practical details of the subject. The Transportation Division is also prepared to take up with shippers many other details bearing on this subject, such as preparation of shipping documents, correct classification in order to secure most favorable transportation rates, selection of the proper vessels for most direct deliveries, correct ports of entry, avoidance of lighterage and trans-shipments, where possible, and many other details. American shippers of dyestuffs and dyes-making materials owe it to themselves to take advantage of the assistance and cooperation of the Transportation Division.

Coal tar products and the finished dyes are handled in most of the Latin-American countries by "farmacias," chemical houses and wholesale drug concerns (distributors). In some of the larger cities, such as Buenos Aires, Argentina; Rio de Janeiro, Brazil; Montevideo, Uruguay; Valparaiso, Chile; Mexico City, Mexico; Havana, Cuba, and some others, there are import commission dealers who handle a large number of imported products on a commission basis. Many of these carry American dyes and have large clienteles. An important point to remember, however, is that our manufacturers using these go-betweens should exact an agreement that no competing lines be handled. The necessity for this is obvious.

Finally, we have to the south of us a trade field of approximately 120,000,000 people — a population almost equal to that of the United States—who are looking to this country at this time as never before to supply their dyes and materials, practically none of which are produced in Latin America. Another very important fact upon which we cannot place too much emphasis is that the people of these countries have a fondness for colors of the widest possible range. This comes naturally as a racial trait of both the Indian residents, the Spanish and the Portuguese. As a matter of fact color is carried to an extreme not approached in any other part of the world. Such a trade field, it must be conceded, offers opportunities well worth cultivating.

New Carbic Pattern Card

The Carbic Color & Chemical Company has recently issued a new pattern card entitled "Indigisol Prints on Cotton Material." This card illustrates all the indigosols brought out so far with the exception of the recently introduced Indigosol Grey IBL. The colors are shown printed in two depths and complete details concerning the methods of application and fastness qualities are given. Copies of this card may be obtained on request.

TEXTILES IN THE THEATRE*

By **F. G. H. Macrae**

(*Chief Engineer, Theatre Royal, Drury Lane, W. C. 2*)

FOR many years draperies have formed part of the theatre decoration particularly in the auditorium. A change in the method of scenic design led to their use also on the stage in the form of curtains, wings, and borders. The important aid they gave to effective lighting has been the means of them being employed still more in connection with stage spectacle.

Velour Scenery

Built scenery has for some time consisted of a wooden structure covered with canvas on which the artist paints the design. In some recent productions the canvas has been replaced by velour—usually white or cream colored—which is tacked to the woodwork. The advantage of this is the wonderful effects obtained by lighting, due not only to the skill of the artist, but also to the effect of the nap of the material, which has the property of reflecting the light according to the angle of projection. Sometimes the artist teases the material in order to get different gradations of light, and for exterior scenes and woodland designs the result justifies the additional expense.

Color Experiments

The cinema has displayed considerable ingenuity in the combination of lighting and fabrics, and hitherto it has been left to a few firms who specialize in theatre work to study the various effects. Experiments have shown that many original displays may be possible by varying conditions during the process of manufacture and dyeing, and the textile trade might find it beneficial to give a thought to experiments in this direction. An experimental color lighting apparatus need only consist of three small flood lamps with the primary colors of light—red, blue, and green. If each lamp is fitted with a dimmer, hundreds of grades of color can be produced by mixture of the three lights.

Fluorescent Fabrics

Another stage effect with draperies and costumes which is finding favor in this country is the use of the ultra-violet rays on materials chemically treated. Described briefly, it is achieved by arc lamps fitted with a glass filter which cuts off nearly all the visible light and transmits the short waves of ultra-violet. When these impinge on a material treated with dyes such as eosine, fluorescein, auramine, and others, a fluorescence is produced which is similar to a phosphorent light. Here the help of the textile manufacturer is needed since some materials respond to treatment while others give no effect at all. Research in this direction seems to have been neglected principally on the grounds that the market does not justify experiments, yet thousands of pounds annually are spent by theatres who are ever on the lookout for originality.

The subject has been developed in Germany and America and orders have been sent to these countries which should have been placed at home. There appears to be no technical reason why a material should not be dyed to produce fluorescence in the first place without having to be treated a second time, and so avoid spoiling the original color under ordinary light. The present method with costumes is to spray them, resulting in a patchy effect, especially in the folds of the garment. It is possible to treat white silk and lace with a colorless solution which under ordinary light allows them to retain their whiteness, but changes them to a wonderful blue under the ultra-violet rays. The process has long passed the stage of a mere trick, whole scenes and hundreds of costumes have been treated, entailing considerable expenditure.

Fire Risk

Most licensing authorities require permanent curtains to be incombustible and specify heavy woollen material. In the case of stage draperies they should be opaque so that light behind is not transmitted through them. Sometimes they are backed with a material which fails to pass the fire test in which case they are liable to be condemned.

Gauze is used very considerably in theatrical production and is fireproofed by being dipped in a suitable solution, a method which sometimes has disastrous results especially on linen cloths painted with aniline dye—a favorite practice with many continental artists. Very light material like Jap silk will not hold the fireproofing for long, and must be re-dipped at frequent intervals.

*The Textile Manufacturer.

Calgon—A New Agent for the Improvement of Laundering

It has been found in a joint investigation of the Buromin Company of Pittsburgh, Mellon Institute, and the American Institute of Laundering that *Calgon,* a new phosphate, possesses distinct utility in laundering processes.

According to the report on this research, Calgon has the unique property of dissolving lime soaps by transforming them into active sodium soaps. The utilization of ths property in the washing formula is said to represent a real innovation in laundering methods, because it enables the removal of lime soaps as an integral part of the washing formula. The occurrence of lime soaps in soft-water laundries is pointed to as far more widespread than is commonly thought. It was proved that Calgon is not injurious in any way to textile fabrics nor to colors, and that its use effects an economy in washing supplies.

Copies of the complete report are procurable gratis upon application to Mellon Institute of Industrial Research, Pittsburgh, Pa.

The Dyeing of Viscose Yarns*

By J. BOULTON, A. E. DELPH, F. FOTHERGILL, and T. H. MORTON

(*Courtaulds Limited*)

WHILE much work has been done on the physico-chemical nature of solutions of the dyestuffs, very little accurate quantitative work appears to have been done on the absorption of dyestuffs by cellulose. An attempt has been made to study the process of dyestuff absorption by cellulose, usually in the form of viscose yarn, in a strictly quantitative manner, and below a summary of the results so obtained is given.

Commercial dyes may, and in general do, contain large quantities of organic and inorganic impurities and diluents, which must be removed in order to obtain a material suitable for quantitative investigation. Two essential requirements have first to be met—

(1) The employment of suitable dyestuffs in a chemically pure state.

(2) The development of methods for determining the purity of these dyes and for their convenient estimation in the course of absorption experiments.

The three colors chosen for the present work were Benzopurpurine 4B (Colour Index, No. 448) and Sky Blue FF (No. 518), representative of the unlevel dyeing direct dyes, and Chrysophenine G (No. 365), representative of the level dyestuffs. Also their molecular constitution is well established. The dyes were first repeatedly salted out from aqueous solution by means of sodium acetate. Removal of electrolyte was followed by recrystallization from aqueous alcohol in the case of Benzopurpurine 4B and Chrysophenine G, and by extraction with alcohol in the case of Sky Blue FF.

Measurements of sufficient accuracy of the concentration of solutions of dyes have been found possible with a Klett colorimeter of the Dubosc type. In a simple dyeing the amount of dyestuff absorbed is easily determined by an estimation of the residual dye in a carefully prepared dyebath. There is, however, a more complicated absorption system in which two yarns are dyed simultaneously in the same bath. To meet this case the dyestuff is stripped quantitatively from the fiber by extractions with hot 15% aqueous pyridine and estimated colorimetrically. Chrysophenine G, however, is rapidly and completely stripped from yarn by hot water alone.

In conducting dyeing experiments capable of duplication it is essential to maintain an accurate control of temperature and to prevent evaporation.

In the earlier days of the rayon industry it was assumed that all direct cotton colors would be suitable for use with viscose yarns, but this was soon observed not to be the case. C. M. Whittaker has not only classified a large number of dyes but has also devised several methods for a rapid determination of the dyeing properties of any dye. Two important facts emerge from this work which must be explained by a complete theory of the dyeing process.

(1) In dyeing for a fixed time those dyes which show a maximum affinity at a low temperature are level dyeing, while those which show a maximum affinity at a high temperature (90°) are the most unlevel.

(2) The dyeing process is more rapid at a given temperature with a level than an unlevel dyestuff.

It is clear that time is an important factor in the dyeing process.

Dyeing Kinetics of Rayon

A series of absorption-time curves has been obtained for the three pure dyestuffs on three viscoses of varying filament denier, a fine filament stretch-spun Lilienfield viscose yarn, and a stretch-spun cuprammonium yarn. A typical set of absorption curves is given in Figure 1, which refers to the absorption of Chrysophenine by a 300/36 (300 denier, 36 filaments) viscose. These curves are similar in shape to those obtained for all the yarns with the several dyestuffs.

Several important points emerge from a study of this series of curves.

(1) For any one curve, where temperature, yarn, and initial composition of the dyebath are maintained constant, the absorption velocity decreases with increasing time, until an equilibrium absorption is reached. This equilibrium, dependent on the composition of the bath, may be reached when little or practically all the dye originally present has been absorbed.

(2) The speed of attaining this equilibrium with other conditions constant, varies with the yarn. If curves are

*Abstract of paper, "Quantitative Research on the Dyeing of Viscose Yarns," read to the Textile Institute Annual Conference. Reprinted from the *Textile Manufacturer*.

plotted with a logarithmic time scale those for different yarns are similar in shape, being merely displaced on the time scale. The kinetics of dyeing are therefore similar for all the yarns, differing only in a velocity factor. The shapes of the curves are similar to that given by Hill for a process of true diffusion into a cylinder of material from a solution of constant concentration, suggesting that a diffusion process basically controls the kinetics of dye absorption.

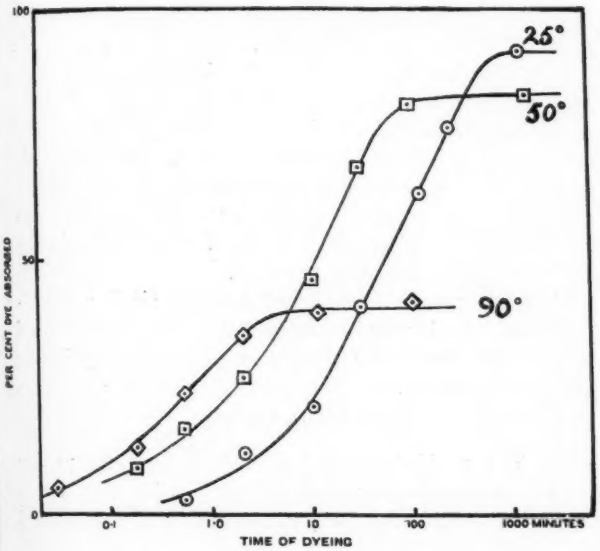

Figure 1.

(3) The observed equilibrium absorption for a given set of conditions is virtually independent of the yarn employed. It is probably permissible to generalize from these results and to state that the *equilibrium* affinities for direct dyes of all normal regenerated cellulose rayon yarns is very nearly identical.

(4) The speed of dyeing varies considerably from one yarn to another.

(*a*) The speed of dyeing is controlled by factors in additions to the relation of surface to bulk of the filaments of the yarn. The enormously greater speed of dyeing of stretch-spun cuprammonium yarn is probably related to a peculiarity in its fine structure which will be referred to later. Preston has demonstrated the existence of a tough, highly oriented "skin" on yarn. All dyestuff passing to the interior of the yarn must necessarily pass through the tough outer zone, which may be expected to vary in properties and extent from yarn to yarn.

(*b*) The rate of dyeing of unlevel is less than that of the level dyes.

(*c*) The *relative* differences in the dyeing properties of a series of yarns tends to be greater with unlevel than with level dyes.

Absorption and Appearance of Shade

The appearance of a dyed yarn clearly depends on factors other than the dyestuff content of the material, for the light which reaches the eyes is compounded of reflected white light and colored light which has passed through various thicknesses of dyed cellulose before being reflected. A coarse and a fine filament viscose containing exactly the same amount of dyestuff appear as if the former were much more heavily dyed, and it has been often assumed that it had absorbed more color and was therefore possessed of a greater "affinity." This, however, is not so and the effect is purely optical.

A thin undyed knitting of 150/36 yarn appears whiter than one of 150/21 yarn because the former presents a larger number of reflecting surfaces to a ray of light passing through it, reflecting therefore a greater portion of the incident light. Similar knittings folded to many thicknesses will appear identical since they will now possess the same number of effective surfaces, for there is sufficient thickness of fabric to reflect all the light. It is clear, however, that the optical path in the coarse filament yarn, although geometrically similar, is longer than in the fine filament yarn. If now the yarns are dyed with the same amount of color the 150/21 viscose will appear darker since the reflected rays here passed through a greater thickness of dyed material, and have therefore suffered greater selective light absorption. To give the same apparent depth of shade on both 150/21 and 150/36 viscose the selective absorption must be identical in the two cases; that is the ratio of concentrations of dye must be inversely proportional to the lengths of the corresponding paths of the light within the two yarns. This ratio is the ratio of the corresponding linear dimensions and is equal to $1 : \sqrt{21/36}$ or $1 : 0.76$.

The above reasoning depends on the assumption of a geometrically similar outline of cross-section of the two yarns. If the outlines are not similar, it is clear that a yarn with a more indented cross-section will behave visually as a yarn of finer filament denier and conversely.

In considerations of the apparent levelness or unlevelness of dyeings expert opinion agreed that the smallest detectable difference would be found with a medium blue shade. A series of dyeings with Sky Blue FF was prepared and it was found that an expert color-matcher could just detect with reasonable certainty a difference of dye content of 2%. A difference in dye content of 5% seemed to be the smallest plainly distinguishable difference.

Whittaker's Classification of Dyestuffs

C. M. Whittaker has employed two main methods of classification of direct dyestuffs according to their levelling properties. These tests can be justified by the quantitative results found.

(1) The "Temperature Range Test."

Essentially this test consist of dyeing for a fixed period, *e.g.*, 30 minutes, in a dyebath of fixed composition at various temperatures. Level dyes give a maximum depth of shade at low temperatures and unlevel ones at high temperatures.

(2) The "Time Range Test."

This test, which is suitable for the classification of the extremely unlevel dyes, consists in observing the time required at 90° for knittings composed of a fast dyeing 150/36 and a slow dyeing 150/21 viscose to assume an apparent equality of shade, as discussed in the previous section. It is found that a longer period is required as the dye investigated possesses a greater degree of unlevel properties.

A Theory of Dyeing

The fine structure of, say, an oriental cellulose is probably best conceived as a three dimensional network of more or less parallel molecular chains, which are not necessarily straight since free rotation is possible at every glucosidic linkage, but which here and there fall into restricted regions of crystalline conformation. When such a structure is swollen by immersion in water, osmotic forces tend to cause the chains to move apart, but in the crystalline regions this is prevented by crystal forces. In the intercrystalline regions the molecular chains will move apart during swelling until the osmotic forces are just balanced by elastic forces tending to restore the structure to its original configuration. Hysteresis in moisture absorption may be explained by postulating that certain elements of structure are broken down during sorption and are only re-formed during desorption at a lower value of the swelling.

Between the crystallites, in the swollen condition, the molecular chains will form an open network through which small molecules may pass with ease. Large particles such as dyestuff molecules will have difficulty in migrating through these capillary spaces and will therefore diffuse slowly.

In cuprammonium yarn, as distinct from viscose, molecules of dyestuff are able to penetrate the unswollen material. Here the cellulose probably contains preformed capillary pores due to some special condition in the coagulation process.

In the normal cellulose structure the molecular chains in the intercrystalline regions and on the outer surface of the crystallites may be supposed to be ready to form molecular compounds by reason of the potential co-ordinating power of the three free hydroxyl groups attached to each glucose residue.

The substantivity of the direct cotton dyes is probably to be explained by the formation of co-ordinated molecular compounds between the color molecule and a portion of the long molecular chain of cellulose. The dye molecules, therefore, must, like the cellulosic molecular chains, be oriented with their long axes parallel.

Immediately the yarn is immersed in the dye bath the outside of the filament absorbs dye until it is in equilibrium with the solution. This is helped by the imbibition of the fiber; a considerable quantity of water is withdrawn from the bath and the dye dissolved in this is retained at the surface of the filament by a process analogous to ultra-filtration. The equilibrium is dynamic and the dye molecules tend to move from the dyed surface to the undyed interior under the influence of osmotic forces. As the surface loses dyestuff in this way more is removed from the bath to take its place, so that, in effect there is a migration of dye from the bath to the interior of the yarn. This process continues until every portion of the cellulose throughout its bulk is in equilibrium with the dyebath.

The speed of dyeing is clearly related to the ease of migration of the dyestuff molecules through the molecular pores of the cellulose structure. The great change in speed of dyeing with small changes in the total swelling of the structure has been illustrated and this suggests again that the pore dimensions are of the same order as the dimensions of the dyestuff molecule. It is probable that the fundamental difference between level and unlevel dyes is that the molecules of the latter diffuse with comparatively much less ease than the former through the fine pores of the cellulose structure.

Since all rayons investigated possess similar equilibrium affinities it may be assumed that the proportion of molecular chains in the cellulose available for dyeing is similar in all cases.

Summary of Paper

(1) The purified direct cotton dyes, Benzopurpurine 4B, Chrysophenine G, and Sky Blue FF, have been employed in a quantitative study of the dyeing of regenerated cellulose yarn.

(2) Dyeing proceeds to an equilibrium which is practically independent of the nature of the yarn.

(3) The principal difference between various rayons, and between light and dark dyeing yarn of the same denier, is to be found in dyeing speed.

(4) Treatment of viscose with caustic soda, prolonged heating, and degradation by acids, affects the speed of dyeing but not the equilibrium finally attained. Degradation by oxidation with hypochlorite substantially decreases the amount of dye absorbed at equilibrium.

(5) The level dyeing dyes as a class are absorbed more rapidly to equilibrium than the unlevel dyes.

(6) The kinetics of dyeing may be explained as a diffusion process. The rate of diffusion of unlevel dyes within cellulose is less than that of the level dyes.

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